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17/20, 17/21(74) Agent: HYTA, Robert, C.; Wells St. John, P.S., 601 W.
1st Avenue, Suite 1300, Spokane, WA 99201-3828 (US).

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Delaware Avenue, Suite 1269, Wilmington, DE 19801
(US).

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(72) Inventors: IKUBO, Yuichi; 2825 Barlow Street, West Lafayette, IN 47906 (US). OWENS, Stephen; 327 Deer Creek Trail, White Pine, TN 37890 (US). COHN, Mitchel; 3029 Couthouse, Apt. 2B, West Lafayette, IN 46205 (US). BRANDSTADTER, Stephan, M.; 3946 N. Washington Boulevard, Indianapolis, IN 46205 (US). HEDRICK, Vicki, E.; 9262 South 300 E, Brookston, IN 47923 (US). BOGGS, Janet, K.; 6922 N 900 E, Brownsburg, IN 46112 (US). CHENGPING CHIEN, John; 3384 Peppermill Drive, Apt. 1D, West Lafayette, IN 47906 (US). SACARIAS, Julie; 908 West 7th Street, El Dorado, AR 71730 (US).

(54) Title: MATERIALS AND METHODS FOR THE PRODUCTION AND PURIFICATION OF CHLOROFLUOROCARBONS AND HYDROFLUOROCARBONS

(57) Abstract: Methods and materials are provided for the production of essentially isomerically pure perhalogenated and partially halogenated compounds. One embodiment of the present invention provides a process for the production of essentially isomerically pure CFC-216aa. Other embodiments include processes for the production of CFC-217ba and HFC-227ea. Particular embodiments of the present invention provide separation techniques for the separation of chlorofluorocarbons from HF, from other chlorofluorocarbons, and the separation of isomers of halogenated compounds. Still other embodiments of the present invention provide catalytic synthetic techniques that demonstrate extended catalyst lifetime. In other embodiments, the present invention provides catalytic techniques for the purification of isomeric mixtures.

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MATERIALS AND METHODS FOR THE PRODUCTION AND PURIFICATION OF

CHLOROFLUOROCARBONS AND HYDROFLUOROCARBONS

FIELD OF INVENTION

5 The present invention is directed to synthetic production methods, as well as, synthetic and physical separation methods. More particularly the present invention is directed to methods for efficiently manufacturing selective isomers of chlorofluorocarbons and hydrofluorocarbons from aliphatic, olefinic or partially halogenated hydrocarbons.

10 BACKGROUND OF THE INVENTION

Since the beginning of global warming concerns, chlorofluorocarbon manufacturers have had to produce compounds that perform substantially the same as fully halogenated chlorofluorocarbons without the adverse environmental impact. Only through the introduction of these new compounds have their environmental impact been completely understood. In certain instances, some of these new compounds have been removed from the marketplace. These types of issues make the flooding agent, extinguishing, propellant and refrigerant production industry a dynamic and ever-changing marketplace where processes for the production of chlorofluorocarbons and fluorocarbons are advancing quickly to accommodate both environmental as well as economical requirements.

Some useful compounds in this area include both saturated and unsaturated fluorocarbons, such as 1, 1, 1, 2, 3, 3, 3-heptafluoropropane ($\text{CF}_3\text{-CFH-CF}_3$, HFC-227ea), 1, 1, 1, 2, 2, 3, 3-heptafluoropropane ($\text{CF}_3\text{-CF}_2\text{-CHF}_2$, HFC-227ca) and hexafluoropropene (hexafluoropropylene, HFP, $\text{CF}_3\text{-CF=CF}_2$, FC-1216). One well known method of synthesizing these compounds begins with the chlorofluorination of propane, propylene or partially halogenated C-3 hydrocarbons with hydrogen fluoride (HF) and chlorine (Cl_2) in the presence of a metal-containing solid catalyst. Examples of this chlorofluorination step can be found in U.S. Patents 5,057,634 and 5,043,491 to Webster. As taught by Webster, the chlorofluorination step produces a number of saturated perhalogenated chlorofluorocarbons, including: (A) $\text{C}_3\text{Cl}_5\text{F}_3$; (B) $\text{C}_3\text{Cl}_4\text{F}_4$; (C) $\text{C}_3\text{Cl}_3\text{F}_5$; (D) 1,2-dichlorohexafluoropropane ($\text{CF}_3\text{-CClF-CClF}_2$, CFC-216ba); (E) 2,2-dichlorohexafluoropropane ($\text{CF}_3\text{-CCl}_2\text{-CF}_3$, CFC-216aa); (F) 1-

chloroheptafluoropropane ($\text{CF}_3\text{CF}_2\text{CClF}_2$, CFC-217ca); (G) 2-chloroheptafluoropropane ($\text{CF}_3\text{CClF}_2\text{CF}_3$, CFC-217ba); and (H) octafluoropropane ($\text{CF}_3\text{-CF}_2\text{-CF}_3$, FC-218). While the FC-218 is useful and can be separated from other perhalogenated reaction products, it is not an efficient or economical intermediate in the synthesis of HFC-227ea, HFC-227ca or FC-1216. As indicated in the '491 patent, the predominant reaction products resulting from the chlorofluorination of propane with HF and Cl_2 is CFC-216aa, which is fluorinated and then dehalogenated to hexafluoropropene (FC-1216).

Due primarily to environmental as well as toxicological concerns, demand is increasing for isomerically pure chlorofluorocarbons and hydrofluorocarbons. Teachings such as those described above cannot begin to address these issues and concerns because efficiency of production as well as isomeric purity were not contemplated. Prior art of similar chemistry does not allow for the exclusive production of the HFC-227ea, but only as a mixture or by-product with FC-1216. The unsuitability of FC-1216 for a fire suppressant does not make this a viable or efficient route.

A need exists to develop a method of chlorofluorinating inexpensive C-3 reactants that eliminates one or more by products of chlorofluorination, particularly FC-218 and undesired isomers which cannot be recycled to produce HFC-227ea or HFC-227ca. Moreover, a long felt need exists for extending the lifetime of catalysts used in these reactions.

Furthermore, the reaction products generated from these steps require purification. U.S. Patents 6,018,083 to Manogue and 6,211,135 to Miller respectively teach the partial separation (azeotropes) of chlorofluorocarbons C_3ClF_7 (CFC-217) and $\text{C}_3\text{Cl}_2\text{F}_6$ (CFC-216) from HF. These references demonstrate the practical difficulty of separating reaction product mixtures with conventional distillation techniques. The formation of azeotropes requires the use of subsequent or expensive distillation techniques to produce a pure product that can be used as a final product or as an intermediate reactant. A need remains for processes that separate chlorofluorination reaction products without forming azeotropes.

The present invention provides processes for the chlorofluorination of aliphatic, olefinic or partially halogenated hydrocarbons in the presence of a catalyst that results in the substantial elimination of FC-218 as a by-product in the

chlorofluorination reaction and that efficiently converts the starting material to the desired isomer. The present invention also provides processes for the efficient purification of reaction product streams.

SUMMARY OF INVENTION

One embodiment of the present invention is directed to a process for the manufacture of HFC-227ea, including a novel and highly selective method of preparing a CFC-216aa intermediate by chlorofluorinating C-3 reactants with HF and
5 Cl₂ without the formation of substantial or even detectable amounts of FC-218 or undesired isomers.

In accordance with the present invention, the C-3 reactants are chlorofluorinated in a first step with hydrogen fluoride and chlorine in the presence of a metal containing catalyst at a first temperature. The reaction products from this first
10 step are then fluorinated with hydrogen fluoride at a second temperature resulting in an unexpectedly high yield of CFC-216aa without the formation of FC-218.

One aspect of the present invention is to provide a method of manufacturing a CFC-216aa intermediate by chlorofluorination of C-3 reactants such as aliphatic, olefinic or partially halogenated hydrocarbons having at least three carbon atoms,
15 wherein the process provides new and unexpected selectivity for the CFC-216aa reaction product.

Another aspect of the present invention provides a method of manufacturing a CFC-216aa intermediate for preparing CFC-217ba and subsequently preparing HFC-227ea with excellent selectivity and yield, without the formation of FC-218 or
20 undesired isomers.

Another embodiment of the present invention includes a process step for hydrodehalogenating CFC-217ba to produce HFC-227ea by contacting CFC-217ba with H₂ in the presence of a metal containing catalyst. According to another
25 embodiment of the present invention, the hydrodehalogenation step is provided as just described, with the addition of water to prolong catalyst life.

The present invention also provides a process for separating the isomers HFC-227ea and HFC-227ca by combining the isomeric mixture with a chlorofluorocarbon and subsequently separating the mixture by distillation. In one embodiment the
chlorofluorocarbon is CFC-217ba.

30 Another process according to the present invention provides for the purification of halogenation reaction products into HF and chlorofluorocarbons. In a more specific embodiment, the halogenation reaction product includes CFC-216aa.

Still another process for separating halogenation reaction products is provided wherein the reaction products are combined with water and cooled to a sufficient temperature to form a gas phase and top and bottom liquid phases. According to this embodiment, the gas phase contains primarily C-3 chlorofluorinated compounds
5 having at least six fluorine atoms, the top liquid phase is primarily an aqueous liquid phase and the bottom liquid phase contains C-3 chlorofluorinated compounds having less than six fluorine atoms.

An additional process according to this invention provides for separating C-3 chlorofluorinated compounds from a halogenation reaction product. One
10 embodiment of this invention includes the adjustment of a halogenation reaction product to a sufficient temperature to separate the reaction product into three phases; an upper gas phase and top and bottom liquid phases wherein the upper gas phase contains primarily HCl, the top liquid phase contains HF and the bottom liquid phase contains essentially acid-free C-3 chlorofluorinated compounds;

15 In still another process of the present invention methods are provided for synthetically increasing the isomeric purity of a mixture. According to one embodiment, an isomeric mixture of C-3 chlorofluorinated compound isomers is heated in the presence of a catalyst to a sufficient temperature to increase the isomeric purity. In a more specific embodiment, the C-3 chlorofluorinated compound isomers
20 are CFC-217ba and CFC-217ca.

In still another embodiment of the present invention a process is provided for selectively halogenating isomers within an isomeric mixture. In a particular embodiment, the isomeric mixture is exposed to Cl_2 in the presence of a catalyst at a sufficient temperature to halogenate at least one isomer. Preferably the isomeric
25 mixture includes the isomers HFC-227ea and HFC-227ca.

The above and other embodiments, aspects, alternatives and advantages of the present invention will become more apparent from the following detailed description of the present invention taken in conjunction with the drawings.

DESCRIPTION OF THE FIGURES

Figure 1 is a schematic representation of one embodiment of the present invention.

Figure 2 is a graphical representation of the isotherms observed during the
5 processes of the present invention.

Figure 3 is a block diagram of an embodiment of Step I according to the present invention.

Figure 4 is a block diagram of an embodiment of Step II according to the present invention.

10 Figure 5 is a block diagram of an embodiment of Step III according to the present invention.

Figure 6 is a block diagram of an embodiment of Step IV according to the present invention.

15 Figure 7 is a graphical representation of the increased catalyst life observed in an embodiment of Step IV performed according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to the embodiments illustrated in the drawings and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended. The invention includes any alterations and further modifications in the illustrated devices and described methods and further applications as would be conveyed thereby to one skilled in the art to which the invention relates.

Referring now to Fig. 1, this invention provides processes for the production of chlorofluoropropanes and fluoropropanes from aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms. Other embodiments of this invention provide specific processes for hydrodehalogenating, isomer and reaction product purification. Selected embodiments of this invention will be described in turn beginning with the broad chemical process steps used to produce selected chlorofluorocarbons and fluorocarbons.

In part, this invention stems from the discovery that the majority of the isomer in the final chlorofluorocarbon or hydrofluorocarbon product originates as an undesired isomer which forms in the initial reactions. This isomer and its downstream counterparts are passed to subsequent reactions undergoing the same chemical transformation as the desired isomeric material. Fortunately, CFC-216ba and its downstream counterparts, have different reaction profiles allowing for their reduction with each subsequent step. Unlike CFC-217ca and HFC-227ca, CFC-216ba is not a "dead end" isomer. A majority of this material is directly converted to the desired isomer CFC-217ba in subsequent steps performed in accordance with the present invention.

Without being confined to any theory, the formation of the undesired isomer takes place in these early reactions by the premature fluorination of the geminal C-2 carbon of aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms. The production of CFC-216ba is but just one example of this type of chemistry.

Referring now to Fig. 2, formation of excess amounts of CFC-216ba in Step I has been observed when the reaction is allowed to exotherm excessively. The large amounts of energy released during this exotherm are probably the ultimate reason for

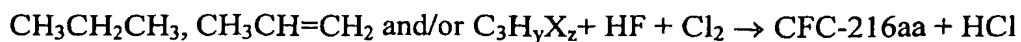
excess CFC-216ba isomer formation. When these types of conditions are allowed to prevail, ratios as low as 2:1 CFC-216aa:CFC-216ba can be observed in these early reaction streams.

During the course of the present invention, it was discovered that one way to control this phenomenon was to carefully operate the initial halogenations so as to avoid uncontrolled exotherms. The reactor used according to the present invention has the ability to use cool heat transfer oil and includes conventional chemical and engineering controls to insure suppression of exotherms. In another aspect of the present invention, HF can be replaced as the main diluent for the reaction. Figs. 3-4 show a schematic flow diagram for a process according to the present invention that includes a two temperature zone chlorofluorination of a C-3 reactant selected from propane, propylene, partially halogenated C-3 acyclic hydrocarbons, and mixtures thereof, with hydrogen fluoride and chlorine in the presence of a chlorofluorination catalyst. The process is highly selective in the production of CFC-216aa, without the formation of any significant amount of FC-218(0 to less than 0.5 percent by weight). The high yield and selectivity of the process of the present invention in the synthesis of CFC-216aa is very advantageous for the subsequent production of HFC-227ea as discussed below.

The present invention provides two step processes for efficiently producing CFC-216aa. The chemical steps are the sequential replacement of hydrogen with chlorine and the subsequent partial replacement of chlorine with fluorine atoms. Multiple products are formed with intermediate fluorinated materials being the majority. Careful temperature control minimizes by-product formation. Typical reaction products include C-3 molecules with 2 to 7 fluorine atoms, the rest being chlorine. The cracking of the C-3 backbone to form C-1 and C-2 materials as undesired impurities is also observed. According to one embodiment, the output of Step I will be fed directly into Step II as shown in Fig. 4, which is run at a higher temperature.

Individual reactants may be fed under flow control to vaporizer(s) 14, as shown in Fig. 3. The vaporized chlorine and HF are mixed and fed into a superheater of Step I. It has been determined that careful mixing of the reactants and temperature regulation helps to control reaction exotherms and lack of control leads to the formation of undesired by-products arising from cracking the C-3 backbone.

The predominant reaction occurring in chlorofluorination Steps I and II can be summarized, as follows, with high selectivity in the production of CFC-216aa:



(X = halogen; y = 0-8, z = 8-y; or y = 0-6, z = 6-y).

5 The process includes a first step wherein C-3 reactants selected from the group consisting of aliphatic, olefinic or partially halogenated hydrocarbons having at least three carbon atoms are contacted with Cl_2 and HF in the presence of a metal containing catalyst. As illustrated in Fig. 3, this reaction is preferably performed in the gas phase by the careful mixing of C-3 reactants with a mixture of hydrogen
10 fluoride (HF) and chlorine (Cl_2) in the presence of a metal containing catalyst at a sufficient temperature to form perhalogenated compounds.

In one embodiment of the present invention, the C-3 reactant is selected from the group consisting of aliphatic, olefinic and/or partially halogenated hydrocarbons, premixed with a mixture of hydrogen fluoride, and then mixed with chlorine before
15 entering chlorofluorination reactor 16 containing a fixed bed of metal containing catalyst.

Aliphatic hydrocarbons having at least three carbon atoms are known in the art as alkanes. These types of compounds include propane. Olefinic hydrocarbons having at least three carbon atoms are known in the art as unsaturated aliphatic
20 hydrocarbons having at least one double bond. These types of compounds include propene. Partially halogenated hydrocarbons having at least three carbon atoms are known in the art as aliphatic or olefinic hydrocarbons wherein one or more hydrogens have been replaced by halogens.

According to one embodiment of the present invention, the HF and C-3
25 reactants are premixed before being combined with the chlorine gas and conveyed into a chlorofluorination reactor. It is preferred to premix (dilute) the C-3 reactant with the hydrogen fluoride reactant prior to combining the HF/C-3 gas reactants with the chlorine gas reactant in order to minimize the potential reaction of the C-3 reactant, e.g., propane and/or propylene with concentrated chlorine gas. Accordingly,
30 at least one of the C-3 reactant or the chlorine, preferably both the C-3 reactant and chlorine, should be diluted with hydrogen fluoride prior to combining the C-3 reactant with the chlorine gas.

In one embodiment of the present invention the HF is anhydrous. It has been determined that recycled or reagent grade HF may be used. The type of HF used to perform this aspect of the invention is not critical and specific types and qualities will be recognized by those skilled in the art. The Cl₂ likewise is a matter of choice to those having skill in the art. In one embodiment, technical or pure-grade anhydrous Cl₂ is utilized.

The chlorination of aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms is a highly exothermic reaction which may be controlled through the use of excess quantities of hydrogen fluoride, a diluent, or an external heat transfer medium together or in combination, to absorb the heat evolved and to maintain temperature control of the mixture.

To reduce the impact of exotherms, preferably, a stoichiometric excess of hydrogen fluoride is maintained in order to minimize decomposition of the C-3 reactant to C-1 and C-2 by-products, and the formation of the less desired CFC-216ba, preferably about 6 to about 64 moles of HF per mole of C-3 reactant. It is preferred to provide an excess of chlorine gas as well, preferably about 8 to about 10 moles of Cl₂ per mole of C-3 reactant, but an excess of Cl₂ is not required. In a preferred embodiment, the ratio of Cl₂ to C-3 reactants can be 8.2:1. The molar ratio of HF to Cl₂ is from about 0.75:1 to about 8:1. Preferably, the molar ratio of HF to Cl₂ is about 4:1. Moreover, in another embodiment a diluent may be added to the reaction to decrease undesired isomer and formation of cracking materials.

Preferably the chlorofluorination reactor 16 used to perform this invention is maintained at a reaction pressure of about 1 Pa to about 53 Pa, preferably about 1 Pa to about 53 Pa and at a temperature in the range of about 150°C to about 450°C, and preferably about 220°C. For best results, residence time in chlorofluorination reactor 16 should be in the range of about 0.5 seconds to about 30 seconds and preferably about 5 to about 10 seconds. The resulting reaction mixture coming out of Step I shown in Fig. 3 is rich in C₃Cl₄F₄ and C₃Cl₃F₅ but will also contain CFC-216aa and many other under fluorinated compounds. Preferably reaction products of this first step are conveyed directly to Step II, as shown in Fig. 4, however it is recognized that the reaction products of Step I, as shown in Fig. 3, may be further purified or supplemented prior to continuing on to Step II. A main goal in Step II is the selective fluorination of these under-fluorinated compounds to the desired isomer CFC-216aa.

The second step in this process replaces all of the terminal chlorine substituents with fluorine to produce CFC-216aa. According to one aspect of the present invention this is accomplished through the use of high temperature reaction conditions, excess HF, and a metal containing catalyst.

5 As shown in Fig. 4, the Step I reaction stream is directly fed into a superheater 24. Optimally, this stream is then fed to Step II reactor 26. Again, as before in Step I, careful temperature regulation is used to control the reaction.

The second reaction can take place either in the same reactor as Step I or, preferably, in a second reactor. The second step is carried out at a higher temperature
10 than the first step with a stoichiometric excess of hydrogen fluoride. According to one embodiment a stoichiometric excess of chlorine can be used to ensure chlorofluorination of the Step I reaction products.

Preferably, Step II reactor 26 is a fixed-bed reactor having a metal containing catalyst, maintained at a reaction pressure of about 1 Pa to about 53 Pa and preferably
15 about 8 Pa, and at a temperature higher than the temperature required in Step I. Step II occurs at a temperature ranging from about 300°C to about 550°C, and preferably at about 470°C. It is preferred that the molar ratio of reactants in Step II, should be maintained at about 6 to about 64 moles of hydrogen fluoride per mole of perhalogenated compounds. As in Step I, the source and quality of anhydrous HF
20 used in Step II is not critical. It is to be understood by those skilled in the art that anhydrous, recycled, and/or differing grades of HF can be used in Step II. As in Step I, a diluent may be added to control exotherms and increase isomeric yield.

The metal containing catalyst used in Step I or Step II can be any known catalyst useful for reacting C-3 reactants or perhalogenated compounds with HF
25 and/or Cl₂, including those described in U.S. Patent Nos. 5,177,273 and 5,057,634 to Webster, hereby incorporated by reference. These catalysts include catalysts consisting essentially of chromium; catalysts consisting essentially of chromium oxide in combination with a support (e.g. refractory oxide); catalysts consisting essentially of chromium oxide modified with up to about 10 percent by weight based
30 upon the weight of chromium in the catalyst of metal selected from the group consisting of manganese, iron, cobalt, nickel, copper, zinc, other metals and mixtures thereof; and catalysts consisting essentially of chromium oxide in combination with a refractory oxide and modified with up to about 10 percent by weight based upon the

weight of chromium in the catalyst of metal selected from the group consisting of manganese, iron, cobalt, nickel, copper, zinc, other metals and mixtures thereof. Chromium oxide catalysts and their preparation in the art of perhalogenation are well known.

5 The chromium oxide and metal modified chromium oxide catalysts may be unsupported or supported. Catalysts consisting essentially of either chromium oxide or metal modified chromium oxide in combination with a support (e.g., alumina) may be prepared by conventional procedures (e.g., impregnation of the support using a
10 suitable soluble chromium salt alone or in combination with a suitable soluble salt of the metal modifier). In addition, catalysts of this invention can also be prepared by co-precipitation methods, which are known in the art. Typically for refractory oxide containing catalysts, the refractory oxide constitutes from about 80 to 99.5 weight percent of the catalyst.

 Catalysts consisting essentially of fluorinated chromium oxide, or fluorinated
15 chromium oxide in combination with a refractory oxide, or fluorinated metal modified chromium oxide or fluorinated metal modified chromium oxide in combination with a refractory oxide may also be used. Indeed, the catalysts are preferably fluorinated prior to use for the halogenation process of this invention by treatment with a suitable fluorine-containing compound (e.g., HF, SF₄, CCl₃F,
20 CCl₂F₂, CHF₃, or CCl₂F-CClF₂) at elevated temperatures. Pretreatment of catalysts containing refractory oxides such as alumina are considered particularly useful. Such treatments are well known to the art. The treatment with HF or other fluorine-containing compound can conveniently be done in the same reactor which is to be used for the production of the selected halohydrocarbon product(s). Iron and nickel
25 containing catalysts, specifically iron chloride and nickel chloride catalysts, supported or unsupported may be employed as well.

 The catalysts of this invention can undergo changes in composition and/or structure during use. One skilled in the art will recognize, for example, that during use the catalyst may be in the form of an oxyfluoride, an oxychloride, an
30 oxychlorofluoride and/or an oxide, and/or may have a different crystalline structure from the catalyst charged to the reactor. Charging the reactor with these compounds (e.g., an oxyfluoride, etc.) or with any compound(s) convertible to these compounds

under reaction conditions is considered an equivalent procedure within the scope of this invention.

In this and the other reaction sequences, reaction with HF includes either high temperature vapor phase reaction or lower temperature reaction in the presence of a liquid phase catalyst such as SbCl_5/HF or SbF_5 ; the vapor phase process is preferred.

Two metal containing catalysts that have been found to be particularly useful for the chlorofluorination reactions include:

(1) FeCl_3 on a support, particularly active carbon, that is dried and then fluorinated, e.g., with HF, preferably an HF/N_2 mixture, with or without O_2 , at about 200°C to about 270°C and then treated with HF, with or without O_2 or Cl_2 activation, within the range of about 270°C to about 320°C. It is preferred that the percent by weight of FeCl_3 in the metal containing catalyst be in the range of about 2% to about 36% by weight on a catalyst support, which is preferably activated carbon, preferably at about 5% to about 10% by weight FeCl_3 . It is useful to fluorinate the metal containing catalyst for a period of at least about 2 hours, preferably about 2 to about 16 hours, more preferably about 8 hours, gradually increasing the temperature within the range of from about 200°C to at least the chlorofluorination reaction temperature, e.g., up to about 320°C; and

(2) CrCl_3 , particularly chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) on a support, particularly active carbon, that is dried and then fluorinated, e.g., with hydrogen fluoride gas (HF), in the same manner as fluorination of the FeCl_3 catalyst with or without O_2 or Cl_2 activation.

Non-limiting examples 1, 2, and 3 demonstrate the preparation of catalysts suited for the present invention and non-limiting example 4 demonstrates the activation of catalyst suited for this invention.

Generally, all fluorination catalyst were prepared by mixing appropriate amounts of the selected metal salt and support (if necessary) in DI water. This mixture is allowed to stand for approximately 0.5 hour and the excess water is filtered off by vacuum filtration. The resulting solid is then dried overnight in a gravity oven at 115°C and then charged to the reaction tubes where it is further dried at 150°C with an inert gas purge and then activated with HF before the reaction feeds are started.

Example 1: FeCl₃/Activated Carbon Catalyst Preparation:

Iron (III) chloride hexahydrate (20 grams) was dissolved in deionized water (300 cc). The solution was then mixed into and absorbed by 200 grams of active carbon pellets and air-dried overnight.

5 Example 2: CrCl₃/Activated Carbon Catalyst Preparation:

Chromium (III) chloride hexahydrate (12.6 grams) was dissolved in deionized water (100 cc). The solution was mixed into and absorbed by 75 grams of active carbon pellets and air-dried overnight.

Example 3: NiCl₂/Activated Carbon Catalyst Preparation:

10 Nickel (II) chloride hexahydrate (13.8 grams) was dissolved in deionized water (100 cc). The solution was mixed into and absorbed by 75 grams of active carbon pellets and air-dried overnight.

Example 4: Metal Chloride/Carbon Catalyst Activation Methods:

15 The chlorofluorination catalyst was activated using a chlorofluorination reactor with HF. The following description gives the detailed procedures for three methods of chlorofluorination catalyst activation.

(a) The FeCl₃/carbon catalyst of Example 1 was added to both Step I and Step II reactors and the catalyst in each reactor was dried with N₂ and fluorinated with HF/N₂ to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF mole of active metal in the catalyst at 250°C for 9 hours. The metal containing catalyst in the Step I reactor was then further activated with HF/N₂ to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF per mole of active metal in the catalyst at 285°C for another 14 hours. The metal containing catalyst in the Step II reactor was then further activated with HF/N₂ to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF per mole of active metal in the catalyst at 465°C for another 14 hours.

(b) The same procedure discussed above in method (a) was performed for drying metal containing catalyst with N₂ and fluorination with HF/N₂. The metal containing catalyst was further activated with 2% by weight O₂ along with HF/N₂ to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF per mole of active metal in the catalyst for 12 hours, then another 2 hours without O₂.

(c) The same procedure was performed for the catalyst activation as described above in method (b) except using 2% by weight Cl_2 instead of 2% by weight O_2 .

For all reactions exemplified herein, except where noted, two 41.6 cc, 12.7 mm (OD), Incone® reactor tubes heated with ceramic fiber, radiant heat electric
5 ovens were utilized as reactors. The tubes were utilized alone or in tandem to perform the reaction examples.

Non-limiting example 5 demonstrates the results of chlorofluorination, according to the present invention.

Example 5: Chlorofluorination of C-3 Reactants:

10 Step I was conducted according to the parameters indicated in Table 1 below. The reaction products of Step I were conveyed to the Step II reactor. The Step II reaction was also conducted according to the parameters indicated in Table 1.

Like Step I, Step II was performed with a fixed-bed reactor containing a metal containing catalyst. The specific types of catalyst are described in Table 1 below.
15 The hydrogen fluoride used in Step I and Step II was anhydrous liquid HF that was vaporized to provide anhydrous HF gas. The results of the present example are shown below in Table 1.

Table 1. Step I and Step II with Metal Chloride Catalyst Systems

Catalyst	Reactant Flows HF/Cl ₂ /C ₃ H ₈ (cc/min)	Reactants Mole Ratio (HF/Cl ₂ /C ₃ H ₈)	Step I Run Conditions			Step II Run Conditions			Results*	
			Temperature (C)	Contact Time(sec)	Contact Time(sec)	Temperature (C)	Contact Time(sec)	Contact Time(sec)	%CFC- 216aa	% CFC-216ba
FeCl ₃ / Activated										
Carbon	109.1/44.8/3.2	49/20/1	400	6.4		450	5.8		79.8	nd
CrCl ₃ / Activated										
Carbon	106.5/43.9/2.5	48/20/1	300	7.8		480	5.9		81.9	6.3
NiCl ₂ / Activated										
Carbon	137.3/31.1/2.5	61/14/1	300	7		480	5.3		39.6	8.6

nd = Not detected. *% GC Area

As demonstrated in Table 1 above, iron and chromium chloride catalysts are particularly well suited for use as metal containing catalysts according to the present invention. In particular, when utilizing the iron catalyst no detectable levels of the undesired CFC-216ba isomer were found.

- 5 Non-limiting example 6 demonstrates the reaction efficiency of the present invention.

Example 6: Mass Balance Demonstration:

- Step I was conducted at a temperature of about 280°C with a molar ratio of HF:Cl₂:C-3 reactant, 6:9:1. Residence time in the Step I reactor was about 10
10 seconds. The reaction products of Step I were conveyed to the Step II reactor. The Step II reaction was carried out at about 465°C. Like Step I, Step II was performed with a fixed-bed reactor. The chlorofluorination catalyst used in both halogenation reactors (Step I and Step II) was a supported chromium containing catalyst.

- The reaction products, contained predominantly CFC-216aa, hydrogen
15 fluoride and hydrogen chloride gas, and were conveyed into a central portion of a strip column for HCl removal.

- The chlorofluorination reaction products were collected for analysis by gas chromatography. The amount of the specific compound is indicated in terms of chromatographic area percent. For this, and the following examples, area percent is
20 consistently utilized to demonstrate the advantages of the present invention.

The reaction products were collected for analysis and reported in Table 2 below.

Table 2. Mass Balance of Reactants and Products of the Present Invention

Total Feed Materials	C ₃ H ₈	3.1 kg
	Cl ₂	46 kg
	HF	8.7 kg
Total Products Collected	HCl	41 kg
	C ₃ Cl ₂ F ₆	11 kg
	Underfluorinated compounds	3.4 kg
Recovery		~95%

As Table 2 shows, (mass balance) of the present invention is good at approximately 95% recovery of reactants.

Non-limiting example 7 demonstrates the flexibility of starting material selection of the present invention.

5 Example 7: Use of Varying Starting Materials and Reagent Proportions:

Tandem Incone® pipes were charged with supported chromium oxide catalyst. Liquid HF was vaporized and the HF vapor was then mixed with propylene/propane gas through an in-line static mixer and then mixed with Cl₂ at the top of the Step I pipe, according to the parameters shown below in Table 3. The reaction products from the Step I pipe were conveyed to the Step II pipe and the Step II reaction products were fed into a strip column to separate HCl, Cl₂ and light components from HF, CFC-216aa and heavy components that were removed from the bottom of the strip column. The strip column bottom components were then fed into a phase separator to separate HF from organic materials, including C₃Cl₂F₆ for analysis by gas chromatography. Recovered or recycle HF was fed back to the Step I pipe vaporizer. The underfluorinated organic materials were collected and recycled back to the Step I pipe for further fluorination.

The results of using propane or propene as a C-3 reactant is shown below in Table 3, propene (C₃H₆, Runs A and B) or propane (C₃H₈, Runs C and D) as the raw material (C-3 reactant) for the present invention. The results of using varying proportions of reactants and the effects of additions of a diluent are shown below in

Table 4. The exotherms observed during run conditions dictated in Table 4 are demonstrated in Figure 2.

Table 3. Use of Either Propane or Propylene as a C-3 Reactant

Example	Step I Temp. (°C)	Step II Temp. (°C)	Pressure (Pa)	Flow Rates			Ratio		(moles) Cl ₂ /C ₃ H ₆	G.C.% C ₃ Cl ₃ F ₆
				HF (g/min)	Cl ₂ (g/min)	C ₃ H ₆ (g/min)	HF/C ₃ H ₆			
				Flow Rates			Ratio	(moles)		
A	227.8	465	4.8	29.77	28.38	2.27	27.54	7.40	71.95	
B	275	465	4.8	30.2	31.17	2.12	29.92	8.7	72.21	
				Flow Rates			Ratio	(moles)		
				HF (g/min)	Cl ₂ (g/min)	C ₃ H ₈ (g/min)	HF/C ₃ H ₈	Cl ₂ /C ₃ H ₈		
C	282.5	465	4.8	28.46	31.28	2.02	31.00	9.60	68.38	
D	282.7	465	4.8	30.6	31.02	2.27	29.66	8.47	71.96	

As Table 3 above demonstrates, the present invention is equally efficient regardless of the starting material. It was concluded that the selection of an under halogenated compound as a C-3 reactant will demonstrate similar results.

TABLE 4 - DEMONSTRATION OF UTILIZING VARYING REACTANTS AND DILUENTS

RUN	Diluent (X)	Step I Reaction Parameters				Step II Reaction Parameters				Results		
		TEMP. (C)	CONTACT TIME (seconds)	MOLE RATIO (X:HF:Cl ₂ :PROP.)	MOLE RATIO HF:Cl ₂	TEMP. (C)	CONTACT TIME (seconds)	MOLES HF:PROPANE	% CFC-216aa IN GAS STREAM	% CFC-216ba IN GAS STREAM	SELECTIVITY (%)	
A	none	200	10.2	0:4.7:7.4:1.0	0.64	450	3.7	15.1	51.0	4.16	56.4	
B	CFC-217ba	200	9.7	1.6:4.8:6.3:1.0	0.77	450	3.6	15.2	55.5	5.79	73.8	
C	CFC-217ba	200	10.1	4.0:5.1:7.9:1.0	0.65	450	3.7	19.2	61.6	n/d	87.5	
D	none	200	9.2	0:5.3:4.4:1.0	1.20	450	3.4	13.3	13.17	1.74	32.2	
E	HFC-227ea	200	11.0	4.3:4.6:9.1:1.0	0.50	450	3.9	20	32.01	18.57	69.9	
F	CFC-217ba	260	9.2	2.9:4.4:6.1:1.0	0.72	450	3.7	16.1	72.1	n/d	85.1	
G	none	200	10.7	0:17.5:4.3:1.0	4.04	450	3.9	36.2	39.6	n/d	48.5	

As Table 4 above demonstrates, with particular reference to runs C and F, the present invention is highly selective for CFC-216 aa. As in Figure 2, Table 4 demonstrates the exotherms observed are consistent with the formation of undesired isomers.

In non-limiting example 8 below, the benefit of combining reagents in a specified order according to the present invention is demonstrated.

Example 8: Raw Material Mixing Effect:

Two tests were performed by: (1) using a static mixer to first mix HF with
5 C₃H₈ and then mix the HF/C₃H₈ mixture and Cl₂ in another mixer before the Step I reactor; and (2) first mixing the HF with Cl₂ using a static mixer, and then adding the HF/Cl₂ mixture to C₃H₈ in another mixer before the Step I reactor. The reaction parameters and results of this example are listed in Table 5 below.

Table 5. Mixing Affect on Product Formation According to the Present Invention

Example	Step I Temp. (°C)	Step II Temp. (°C)	Pressure (Pa)	Flow Rates			Ratio	(moles)	C ₃ Cl ₂ F ₆ (GC Area %)
				HF (g/min)	Cl ₂ (g/min)	C ₃ H ₈ (g/min)	HF/C ₃ H ₈	Cl ₂ /C ₃ H ₈	
(a) mixing HF/C ₃ H ₈		(b) mixing Cl ₂							
8A	274.6	465	4.8	34.39	38.09	2.02	37.45	11.69	61.86
8B	274.5	465	4.8	36.40	36.52	1.97	40.65	11.49	60.49
(a) mixing HF/Cl ₂		(b) mixing C ₃ H ₈							
8C	274.8	465	4.8	32.90	35.18	1.89	38.30	11.54	63.01
8D	275.7	465	4.8	32.63	34.62	1.89	37.98	11.35	63.34

As Table 5 demonstrates, the combination of reactants plays no role in the overall selectivity of $C_3Cl_2F_6$. Even though it appears conversion is increased it is probably due to increased residence time in the reactor, rather than order of mixing of reactants.

5 Another process according to the present invention provides for purifying halogenation reaction products. For purposes of the present invention, halogenation reaction products encompass those reaction products as described above and refers to reaction products of reactions wherein chlorine and/or fluorine atoms replace hydrogen or halogen atoms along carbon atom backbones. In most cases the products
10 of these reactions include HF and organic chlorofluorinated compounds. In another embodiment of the present invention the C-3 chlorofluorinated compounds have at least six fluorine atoms.

Referring to Fig. 4, according to one embodiment of the present invention to separate HF from C-3 chlorofluorinated compound reaction products, the temperature
15 of the chlorofluorination reaction product is reduced to a sufficient point within phase separator 28 to separate the reaction products into separate top and bottom liquid phases. According to one embodiment, the temperature used to accomplish this separation is from about -30°C to about -10°C . In a preferred embodiment the temperature is about -20°C .

20 To complete the separation of the HF from the C-3 chlorofluorinated compounds (which can have at least six fluorine atoms) the top phase (formed by lowering the temperature of the chlorofluorination reaction products) is removed to obtain essentially organic free HF and/or simultaneously the bottom phase is removed to obtain essentially acid free C-3 chlorofluorinated compounds. This separation can
25 be performed on an industrial scale continuously in a unit operation or in a batch operation. Persons skilled in the chemical engineering arts will routinely be able to select the type of apparatus necessary to perform this liquid/liquid phase separation.

One of the distinct advantages of this process for separation HF from C-3 chlorofluorinated compounds is that expensive distillation is not required. Nor is
30 there a production of the HF/C-3 chlorofluorinated compound azeotrope. Problems associated with distillation processes and the production of HF/chlorofluorocarbon azeotropes are discussed in U.S. 6,211,135 to Miller, herein incorporated by

reference. Referring now to Figure 4., it has been found during the course of the present invention that at low temperatures, the HF phase 30 is virtually free of organic C-3 chlorofluorinated compounds and likewise the organic phase 32 having C-3 chlorofluorinated compounds are virtually free of HF. Moreover, because the
5 separation according to the present invention results in two product streams, either product may without further purification be sent on to additional reaction steps or returned or recycled to previous reaction steps.

Because the phase separation of the present invention is performed in the liquid phase, any pressure sufficient to maintain the materials in the liquid phase can
10 be used according to the present invention. Preferred embodiments of the present invention use low temperatures and ambient pressures. However, the resulting nonazeotropic mixtures of HF and organic C-3 chlorofluorinated compounds exist at different temperatures depending on the pressure of the system.

The present invention providing for HF/organic separation is demonstrated
15 below by non-limiting example 9.

Example 9: HF/Organic Phase Separation:

A chlorofluorination reaction product including HF, Cl₂ and CFC-216aa was purified according to the present invention. The reaction feed stream included 0.04 kg/s Cl₂, 0.003 kg/s propane, 0.006 kg/s HF and 0.084 kg/s recycled HF with a
20 reaction product stream containing 75 weight percent CFC-216aa on an acid free basis. The HCl was removed by distillation and the bottoms of the distillation column (HF and organic chlorofluorination reaction products) was cooled and sent to a 757 liter liquid phase separation tank where it was chilled. The vapor pressure of the mixture in the phase separator was 1.97 Pa at 21.8°C. The mixture separated into
25 two phases, a bottom phase and a top phase. The bottom phase comprised a liquid organic phase that was decanted off and scrubbed and purified to produce pure CFC-216aa. The top phase comprised a liquid HF phase that was decanted off and recycled to a previous reaction step. The organic phase was analyzed and the results are represented in Tables 6 and 7 below.

30

Table 6. Chlorofluorination Organic Phase Removed from HF According to a
Process of the Present Invention

	Area % Cl ₂	Area % HF	Area % HCl	Area % Organic
Separated Organic Phase	1.21	0.3872	0.6097	97.79

Table 7. Halogenated Organics Separated from HF According to the Present
Invention

Halogenated Organics	Percentage of Total Organics
CCl ₃ F-CClF ₃	not detected
lights	0.05
C ₃ Cl ₂ F ₆	64.59
C ₃ Cl ₃ F ₅	11.82
C ₃ Cl ₄ F ₄	5.75
Heavies	3.65

As this example demonstrates the organic phase, once separated according to an embodiment of the present invention, is essentially acid-free. This allows for the immediate isolation of specific chlorofluorination reaction products without the need for costly and inefficient distillation. Moreover, Table 7 demonstrates that other
5 halogenated organics can be separated from HF according to the present invention. These chlorofluorination reaction products can be isolated according to another process of the present invention as herein described next.

Another process according to the present invention is the separation of the C-3
chlorofluorinated compounds having at least six fluorine atoms from C-3
10 chlorofluorinated compounds having less than six fluorine atoms. This separation process is extremely useful in order to maintain the compound purity of chlorofluorinated compounds sought to be produced.

According to one embodiment of the present process, a solution comprising C-3 chlorofluorinated compounds having at least six fluorine atoms and C-3
15 chlorofluorinated compounds having less than six fluorine atoms is provided. This solution is derived from a reaction product or a refined reaction product of a chlorofluorination reaction or the phase separation or distillation product after a chlorofluorination reaction. In one embodiment of the present invention the C-3 chlorofluorinated compounds having at least six fluorine atoms comprises CFC-
20 216aa. However, this invention is not limited to the source of this mixture.

According to the present invention, the solution is contacted with the water to form a mixture of organics and water. This may be performed using various blending or mixing apparatuses, the particular type of apparatus is not critical and those skilled in the art will recognize apparatus suited for preparing this mixture.

5 It is preferred that deionized water be added to the solution to obtain the mixture. However, other forms of water can be used having various salt concentrations and/or pH levels. According to another embodiment, the water mixed with the solution comprising the chlorofluorinated compounds may include a basic compound, such as potassium hydroxide. Persons having skill in the art will
10 understand that a compound that is basic is a compound that is more alkaline than other compounds. These are known to those skilled in the art as compounds that when added to water raise the pH of the water from its neutral pH to a higher than neutral pH.

 According to one embodiment of the present invention, after mixing, the
15 temperature of this water mixture is then adjusted to a sufficient temperature to separate the water mixture into at least three phases, including an upper gas phase containing C-3 chlorofluorinated compounds having at least six fluorine atoms, a top aqueous phase, and a lower liquid phase containing C-3 chlorofluorinated compounds having less than six fluorine atoms. The temperature sufficient to obtain the three
20 distinct phases described above is from about 25°C to about 75°C. The preferred temperature used to obtain these three phases is about 50°C.

 The above process of separating the C-3 chlorofluorinated compounds alleviates the need for cost intensive and inefficient distillation. The separation of the C-3 chlorofluorinated compounds can be performed as a continuous phase separation
25 process or as a batch phase separation process, applying techniques known to those having skill in the art of phase separation. The upper gaseous phase can be removed to obtain essentially pure C-3 chlorofluorinated compounds having at least six fluorine atoms while at the same time or, alternatively in a batch process, the bottom liquid phase containing C-3 chlorofluorinated compounds having less than six
30 fluorine atoms can be removed either leaving behind or allowing for the removal of the top aqueous phase. Upon removal, these phases can be further processed or retained as end products. According to one embodiment of the present invention, the

chlorofluorinated compounds having at least six fluorine atoms are conveyed to an additional reaction step to increase the number of fluorine atoms present.

Example 10: Separation of Fluorinated Compounds:

The containers of crude $C_3Cl_2F_6$ from various production runs of Steps I and II contained $C_3Cl_2F_6$ and numerous other unidentified underfluorinated compounds, and possible small amounts of H_2O , HF , Cl_2 , and HCl .

Approximately 73 kg of crude $C_3Cl_2F_6$ were fed from a heated cylinder to a 57 liter Halar ® lined scrubber tank. The scrubber tank contained a level gauge and an external heat tracing with a skin temperature thermocouple. The feed line into the tank was through a dip tube.

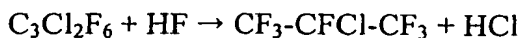
The tank was initially filled with a 5% KOH/water solution and the temperature of the tank was heated to 50°C. The mixture separated into three phases: an upper, primarily gaseous phase; a top liquid, primarily aqueous phase; and a bottom primarily organic phase. The top gas phase was removed as a vapor stream and fed to a Halar ® lined scrubber. The vent gas was open to a molecular sieve dryer bed which fed into a chilled collection cylinder on a scale. Upon completion of the scrubbing of the $C_3Cl_2F_6$, the underfluorinated organics collected from the bottom phase was approximately 9.1 kg of material. The primary components of this organic liquid were $C_3Cl_4F_4$, and $C_3Cl_3F_5$ and $C_3Cl_2F_6$.

Table 8. Results of Separation of Underfluorinated Separation According to the Present Invention

Separated Phase	Constituents
Vapor	essentially pure $C_3Cl_2F_6$
Bottom	~6% $C_3Cl_2F_6$ and ~94% underfluorinated compounds

As Table 8 demonstrates, underfluorinated compounds can be efficiently separated from $C_3Cl_2F_6$ according to the present invention.

Alone or in combination with Steps I and II above, as shown in Fig. 5, the present invention provides a third reaction step (Step III) for the selective fluorination of $C_3Cl_2F_6$ to CFC-217ba. The predominant reaction occurring in this step is as follows:



Preferably, Step III proceeds in the gas phase with excess anhydrous HF over a metal containing catalyst. According to one embodiment of the present invention,

the reactants of Step III are fed under flow control to vaporizer(s) 34. These vaporized reactants include CFC-216aa which are fed to reactor 36.

5 In Step III isomer formation can be controlled by selective fluorination. Since the undesired CFC-216ba contains 2 chlorine atoms it is not technically a "dead end" material. It has been demonstrated that by selective fluorination CFC-216ba will lead to CFC-217ba but CFC-216aa does not readily convert to CFC-217ca. Isomer formation is also effected by conversion.

10 According to one embodiment, the high yield CFC-216aa chlorofluorination product recovered from Step II reaction described previously is mixed with hydrogen fluoride and contacted with a metal containing catalyst. Residence time of Step III is in the range of about two seconds to about 60 seconds, and preferably about 20 seconds to about 30 seconds.

15 Referring to Figure 5, according to one embodiment, reactor 36 is a fixed bed reactor having a metal containing catalyst on a suitable solid support. The metal containing catalyst can be any catalyst known as being useful for the fluorination of C-3 chlorinated hydrocarbons with hydrogen fluoride.

Preferred catalysts for the synthesis of CFC-217ba are supported metal containing catalysts. Metals such as iron, zinc, chromium and mixtures thereof are particularly useful as catalysts for the conversion of $C_3Cl_2F_6$ to CFC-217ba.
20 Acceptable results can be obtained with other metal-containing catalysts, provided the temperature, contact time, and other reaction conditions are suitably selected.

Suitable catalysts are supported catalysts that are dried and HF/N₂ treated at 250°C, e.g., for 9 hours, and then HF/N₂ treated at 465°C, e.g., for another 14 hours using a stoichiometric excess of HF, e.g., about 1.5-3 moles of HF per mole of active
25 metal in the catalyst. This catalyst activation process can include O₂ or Cl₂ gas at a concentration of about 0.5% to about 5% by weight, e.g., 2%.

The catalysts are particularly effective when activated according to one of the following three methods (a), (b), or (c) described below:

- (a) The catalyst is dried with N₂, fluorinated with HF/N₂ at 250°C for 9 hours.
30 The catalyst is then further activated with HF/N₂ at 465°C for another 14 hours.
(b) The same procedure is performed for catalyst drying and fluorination as described above in method (a). The catalyst is then further activated with 2% by weight O₂ along with HF/N₂ for 12 hours, then another 2 hours without O₂.

- (c) The same procedure for the catalyst activation as described above in method (b) is used except using 2% by weight Cl_2 instead of O_2 .

Non-limiting examples 11 and 12 demonstrate the preparation of catalysts suited for the present invention and non-limiting example 13 demonstrates the
5 activation of catalyst suited for this invention.

Example 11: FeCl_3 /Activated Carbon Catalyst:

Iron (III) chloride hexahydrate (3.78) moles was dissolved in deionized water (1000 cc). The solution was mixed into and absorbed by 1000 grams of active carbon pellets and air-dried overnight.

10 Example 12: CrCl_3 /Activated Carbon Catalyst:

Chromium (III) chloride hexahydrate (5.14 moles) was dissolved in deionized water (2100 cc). The solution was mixed into and absorbed by 3000 grams of active carbon pellets and air-dried overnight.

Example 13: Metal Chloride/Carbon Catalyst Activation Methods:

15 The catalyst was activated using a fluorination reactor with HF. The following description gives the detailed procedures for three methods of fluorination catalyst activation.

- (a) The FeCl_3 /carbon catalyst of Example 11 was added to Step III reactor (herein, the reactor is identical to those reactors described previously) and the catalyst
20 was dried with N_2 and fluorinated with HF/N_2 to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF per mole of active metal in the catalyst at 250°C for 9 hours. The catalyst was then further activated with HF/N_2 to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF per mole of active metal in the catalyst at 465°C for another 14 hours.
- 25 (b) The same procedure discussed above in method (a) was performed for metal containing catalyst drying with N_2 and fluorination with HF/N_2 . The metal containing catalyst was further activated with 2% by weight O_2 along with HF/N_2 to provide a stoichiometric excess of HF in the range of about 1.5 to about 3 moles of HF per mole of active metal in the catalyst for 12 hours, then another 2 hours without
30 O_2 .

(c) The same procedure was performed for the catalyst activation as described above in method (b) except using 2% by weight Cl_2 instead of 2% by weight O_2 .

5 The HF:C-3 reactant molar ratio utilized in Step III is preferably in the range of about 1-30 moles of HF per mole of C-3 reactants and the reaction pressure is in the range of about 1-53 Pa, and preferably about 8 Pa at a temperature of about 200°C to about 550°C, and preferably about 485°C. Like Steps I and II previous, Step III may combine a diluent with the reactants.

10 By way of non-limiting example 14, a reaction according to an embodiment of the present invention is shown below.

Example 14: STEP III ($\text{C}_3\text{Cl}_2\text{F}_6 \rightarrow \text{CFC-217ba}$):

A 51 mm I.D. x 1.3 m long Incone® pipe reactor was heated to 485°C by an electric heater. The reactor was connected to a distillation column, which had a pressure control valve to maintain the system pressure at 5 Pa. The reactor was
15 charged with a supported chromium oxide catalyst.

13.88 g/min HF and 6.05 g/min CFC-216aa were fed into a vaporizer. The gas mixture was conveyed to the reactor, and products were removed and fed into a distillation column to separate HCl, CFC-217ba and light components. It is to be understood that the Step III reaction can be carried out using a fluorine-containing gas
20 other than HF.

The heavier Step III reaction products were separated from the CFC-217ba reaction product. The CFC-217ba reaction product included unreacted $\text{C}_3\text{Cl}_2\text{F}_6$. The mass balance results are shown below in Table 9.

Table 9. Mass Balance Results

Total Feed Materials:	$C_3Cl_2F_6$ (99.7%) =	9.4 kg
	HF =	0.9 kg
Total Products Collected:	HCl =	1.2 kg
	HF =	0.13 kg
	C_3ClF_7 =	4.1 kg
	$C_3Cl_2F_6$ =	3.3 kg
Recovery		84.8%

As is demonstrated above in Table 9, approximately 85% of the reactants are recovered as products that can either be further refined, recycled or purified.

Non-limiting example 15 demonstrates the impact of the catalyst selection on the process of the present invention.

5 Example 15: Comparison of Catalyst

The Step III reaction was performed as described in Example 14 above with the exception that the catalyst parameters noted in Table 10 below were utilized. Over a 12-hour period, multiple reaction product samples were taken. The average C_3ClF_7 selectivity is shown in Table 10 below.

Table 10. Average C_3ClF_7 Selectivity % (12 hours average)

Chromium Oxide			Chromium Chloride	
Activated by method (a)	Activated by method (b)	Activated by method (c)	Activated by method (b)	Activated by method (c)
82.74	82.29	84.10	76.19	81.40

10 As seen from these results, the Step III process according to the present invention selectively fluorinates the desired $C_3Cl_2F_6$ resulting in increased C_3ClF_7 production using catalysts of varying chemistry and activation.

To further demonstrate the flexibility of fluorination according to the present invention, numerous catalysts were employed. These catalysts were prepared
15 following the same general preparation methods detailed in examples 1 through 4

described above. These catalyst and reaction parameters are shown below in Table 11.

TABLE II. C ₃ Cl ₃ F ₆ to CFC-217ba with Different Catalyst Systems											
Catalyst	RUN CONDITIONS				RESULTS						
	Contact Temp. (C)	Time (sec)	Mole Ratio C ₃ Cl ₃ F ₆	Conversion CFC-217ba	Selectivity to CFC-217ba	CFC-13	CF-218	CFC-115	CFC-217ba	CFC-114	CFC-216aa CFC-216ba HCF-226da
NiCl ₂ /ZnCl ₂ /AC*	300	27.7	3.2	20.1	1.7	0.08	0.01	0.04	0.34	1.01	71.89
	400	29.6	3	46.5	8.6	18.25	3.81	0.16	3.97	6.81	45.21
	450	18.9	5.3	43.9	85	0.64	0.01	0.07	8.72	0.86	78.92
	480	10.1	5	56.6	90.7	0.81	0.38	0.36	51.23	0.89	43.26
Activated Carbon	300	10.4	6.5	21.0	3.3	0.01	0.00	0.01	0.69	0.64	71.20
	400	19.1	4.2	21.8	51.6	0.13	0.01	0.13	11.22	0.67	72.40
	450	9.2	5.2	14.6	55.7	0.81	0.00	0.09	6.67	0.61	79.36
	480	19.6	5	73.3	91.6	1.24	0.39	0.69	59.86	0.68	30.25
2% FeCl ₃ /AC	400	11.2	6.2	87.6	86.7	0.79	3.74	0.17	70.89	0.35	14.54
	450	10.3	6.2	99.9	35.5	6.88	6.69	1.92	64.62	6.88	0.22
6% FeCl ₃ /AC	300	10.6	6.5	15.3	5.7	0.02	0.00	0.00	0.90	0.49	76.31
	400	19.5	4.2	38.9	74.3	0.16	0.02	0.10	16.08	0.52	72.96
	450	19.5	4	48.4	86.2	0.61	0.16	0.29	35.58	0.60	57.24
	480	19.7	5	89.5	88.4	1.46	0.97	0.76	71.05	0.88	18.69
CrCl ₃ /AC	300	10.5	6.5	52.1	5	0.05	0.00	0.04	2.05	1.63	61.92
	400	20.0	5.7	34.5	71.2	0.44	0.04	0.42	29.85	3.27	59.86
	450	18.9	4	66.4	84.6	0.60	0.13	0.34	39.81	1.53	45.75
	480	18.8	3.8	74.2	84.4	1.81	0.47	0.77	58.97	1.27	26.32
KF / AC	400	19.6	4.2	19.6	34.6	0.23	0.01	0.09	15.10	0.21	63.71
	450	19.6	4	84.3	63.7	1.46	0.40	0.46	77.18	0.55	15.92
	480	19.4	5	79.2	68.4	1.94	1.56	0.66	75.04	0.87	12.23
	480	16.1	2.5	35.2	36.75	3.46	0.07	2.39	12.93	n/d	64.82
Chrome Gel @**	480	18.98	9.5	85.94	84.2	n/d	4.07	0.20	72.36	n/d	14.05

n/d = not detected

*AC = Activated Carbon

**Run in 12.7 mm O.D., 41 cc alloy-600 tube. All other catalyst preparations run in 0.5 in O.D., 34 cc alloy-400 tube.

As the results of Table 11 demonstrate various catalysts and reaction parameters prove useful. Particularly useful are iron, zinc and chromium chloride catalyst systems.

5 The reaction products of the Step III reaction can be purified according to another process of the present invention. A process of the present invention is provided for separating C-3 chlorofluorinated compounds from a halogenation reaction product. The halogenation reaction products contemplated in this invention include the reaction products of Step III described above. This reaction product will include chlorofluorinated compounds having at least three carbon atoms. According to one embodiment of the present invention, the halogenation reaction product 10 includes CFC-217ba. Accordingly, a halogenation reaction product is provided which comprises C-3 chlorofluorinated compounds, HCl and HF. These types of halogenation reaction products will typically result from the halogen exchange of fluorine for chlorine on a chlorofluorocarbon.

15 According to one embodiment of the present invention, the temperature of the halogenation reaction product is lowered sufficiently to separate the reaction products into at least three phases, including a upper gas phase containing HCl, a top liquid phase containing HF and a bottom liquid phase containing essentially acid free C-3 chlorofluorinated compounds. The temperature sufficient to separate the reaction 20 product into at least three phases is from about 20°C to about 75°C. Preferably, the temperature is about 25°C. Like the separations previously described, the particular apparatus used for performing this separation is not critical. Examples of apparatus that would perform sufficiently include temperature regulated tanks and continuous phase separators.

25 The process according to the present invention allows for the continuous and/or batch separation of HF and HCl from C-3 chlorofluorinated compounds. This is desirous in any industrial halogenation reaction scheme or small scale reaction scheme because it is often necessary to remove HCl and HF from the reaction product. Typically, this is a costly endeavor, requiring the separate stripping of the 30 HCl and subsequent distillation of the HF.

Example 16: Heterogeneous Phase Separation of C₃ClF₇:

The fluorination reaction of HF and C₃Cl₂F₆ comprised a reaction product stream containing approximately 40-45 weight % C₃ClF₇ and 50-55 wt % C₃Cl₂F₆ on

an acid free basis. The reaction product was cooled and sent directly to a 3.9 liter liquid phase separation tank. The vapor pressure of the mixture in the phase separator was 6.5 Pa at 25°C. The reaction product separated into three phases. The top gaseous phase was primarily HCl gas. The bottom liquid organic phase was decanted
 5 off to be purified to produce essentially pure C₃ClF₇. The top liquid HF rich phase can be decanted off and pumped directly back as recycled HF, but for purposes of this example, it was discarded. The bottom phase contained mainly organics which measured 54 weight % CFC-216 and 42 weight % C₃ClF₇. The breakdown of the bottom phase composition is shown below in Table 12:

Table 12. Contents of Bottom Phase of Heterogenous Separation

%HF	%HCl	%Organic
1.5	2.5	96.0

10 The top vapor phase gas stream contained primarily HCl and was fed directly to a distillation column for simple distillation. The pressure was controlled for the entire system via this distillation pressure controller to distill HCl out the top. The HF phase composition is shown below in Table 13:

Table 13. Contents of Top Liquid Phase of Heterogenous Separation

%HF	%HCl	%Organic
89.24	4.20	6.56

15 As Table 12 and 13 demonstrate, HF, HCl and organic fluorination reaction products can be efficiently separated in a one-step process. This process is extremely useful because it negates the high costs associated with expensive multi-step distillation and separation techniques.

Once separated according to this invention the reaction compounds can be used as final products or returned to a reaction scheme for further processing.
 20 According to the present invention the compounds thus separated have such high purity that they may proceed immediately to the next step without further purification.

In accordance with still another process of the present invention, a halogenated organic compound is provided to be contacted with H₂ and a catalyst to
 25 form a hydrodehalogenation reaction product. In a preferred embodiment the halogenated organic compounds are the Step III reaction products which include CFC-217ba. Accordingly, the halogenated organic compounds are premixed with hydrogen and contacted with a metal containing catalyst at sufficient temperature to produce a hydrodehalogenation reaction product. In still another embodiment the

hydrodehalogenation reaction products include HFC-227ea. A reaction of this embodiment is shown below:



A slight molar excess of H_2 can be used if desirable but is not necessary. The
5 H_2 :halogenated organic compound molar ratio is in the range of about 0.2:1 to about 10:1, optimally about 1.2:1.

Referring now to Fig. 6, the hydrodehalogenation is performed in fixed bed reactor 42 containing a suitable catalyst, such as palladium on a refractory oxide support, such as alumina or other suitable supports, in which case the reactor is
10 operated at a temperature of about 30°C to about 275°C, and preferably at about 185°C. Alternatively, a ferric chloride (FeCl_3) catalyst on a solid support, such as active carbon can be used in which case the reactor is operated at a temperature of about 200°C to about 600°C, and preferably at about 450°C to about 500°C.

The pressure in reactor 42 should be in the range of about 1.2 Pa to about 15
15 Pa, and preferably about 7.9 Pa. The reaction is largely insensitive to pressure in the range of 0.9 – 7.9 Pa, however, reaction selectivity is slightly favored by lower pressures. Residence time in reactor 42 should be in the range of about 10 seconds to about 90 seconds, and preferably about 15 to about 60 seconds.

While any hydrodehalogenation catalyst could be used, the most active
20 catalysts, such as Pt and Pd, are good selections because, in addition to the desired products, they lead to the addition of hydrogen across any double bond present or to the substitution of hydrogen for chlorine. Catalysts which may be utilized include, as charged to the reactor, common hydrogenation catalysts such as Cu, Ni, Cr, Ru, Rh or combinations thereof. It is not critical whether the catalysts are supported or not.
25 However, supports which are unreactive to halocarbons, HF, and oxygen at hydrogenation temperatures up to 100°C higher such as metal fluorides, carbon, and titania, may be used.

Referring now to Fig. 7, the high cost of noble metals led to concerns regarding catalyst lifetime. Initial testing demonstrated that the catalyst is somewhat
30 fragile with activity dropping off within 5 days. Fortunately, it has been discovered that the addition of a small amount of water to the reaction stream extended catalyst lifetime. The addition of water allows the catalyst to perform in excess of 15 days

with no apparent loss of activity. The chemistry is not particularly sensitive to the amount of water present above a minimum of 0.8%. It has been determined that this process enhancement will test favorably with various catalysts. In one particular embodiment, water was added to the H₂ and halogenated organic compound and contacted with a catalyst. The additional water is from about 0.04 to about 12 percent by weight of the halogenated organic compound, and preferably, about 0.8 percent by weight of the halogenated organic compound. The previous description of the preferred embodiments will now be further demonstrated by way of non-limiting examples.

10 Example 17: Step IV (C₃ClF₇ → HFC-227ea:

 A 12.7 mm I.D. x 0.6 m long stainless steel pipe heated by an electric heater was used to combine materials as described Tables 14 and 15 and Fig. 7 below. The crude organic gas was then washed with water to remove acids and the gas was analyzed by gas chromatography. Table 14 demonstrates the results of this selective hydrodehalogenation with varying catalysts at varying temperatures. Table 15 demonstrates the extension of catalyst life according to the present invention.

Table 14. Hydrogenation of C ₃ ClF ₇ to HFC-227ea with Different Metal and Catalysts Supports							
	Metal Catalyst Loading	Support	Additive	Contact Time(s)	H ₂ /C ₃ ClF ₇	Temp. (C)	% Results – HFC-227ea
							Conversion Selectivity
D i f f e r e n t S u p p o r t s / L o a d i n g	5% Pd	Activated Carbon		16.6	1.5	150	5.8 67.5
						180	16.4 69.5
	1% Pd	Activated Carbon		19.1	2	150	12.2 83.6
						180	47.9 89.8
						200	78.8 91.2
						225	96.8 87.6
						250	99.8 87.0
	1% Pd	Activated Carbon		36.7	1.8	150	26.7 83.5
						180	67.3 90.2
						200	72.0 90.0
						225	92.8 87.1
	0.5% Pd	Activated Carbon		15.4	1	150	3.1 74.4
						180	5.8 66.9
						200	9.6 75.8
	0.5% Pd	Activated Carbon		20.3	2.1	250	45.8 90.2
						275	68.7 88.2
						300	85.5 86.1
						325	95.5 80.0
	2.0% Cu/ 0.6% Pd	Activated Carbon		18.6	2	150	13.4 86.4
						180	50.8 89.3
						200	74.8 87.9
						225	87.6 83.7
						250	97.7 80.7
	2.0% Cu/ 0.6% Pd	Activated Carbon		37	1.8	180	42.7 87.8
						200	67.5 85.4
						225	83.4 85.9
						250	98.3 83.4
	2.0% Cu/ 0.6% Pd	Activated Carbon		10.2	2.4	150	7.1 46.8
						180	15.3 67.5
						200	28.2 76.9
						225	54.0 78.5
						250	80.0 77.9
						275	95.0 75.9
Different Metals	0.5% Ru	Alumina		22.4	1.3	150	2.5 22.4
						180	4.0 32.5
						200	5.0 39.4
	0.5% Rh	Alumina		23.6	1.5	150	12.9 67.1
						180	26.0 77.5
						200	26.6 83.6
	0.5% Pt	Alumina		23.1	1.5	150	2.8 44.5
						180	6.1 50.8
						200	14.3 80.3
Additives	0.5% Pd	Alumina	4.4% H ₂ O	21.9	1.4	180	63.1 98.1
	0.5% Pd	Alumina	1.8% H ₂ O	21.9	1.4	180	73.8 97.2
	0.5% Pd	Alumina	none	22.1	1.4	180	59.5 96.9
	0.5% Pd	#1310 – Alumina	none	21	1.4	180	96.6 95.7

As Table 14 demonstrates, the selectivity of the present invention is substantially the same when performed at less than optimum temperature parameters. This allows for the selective production of selected isomers.

Table 15 and Fig. 7 demonstrate the catalyst life extension effectiveness of the present invention at varying levels of water addition. All conversions represented in Table 15 were performed at 180°C with a H₂ to C₃ClF₇ molar ratio between 0.9–1.5:1, a contact time of 20-30 seconds over a 0.5% Pd on Al catalyst.

Table 15. Catalyst Life Extension

450 ppm H ₂ O	RUN TIME (days)	% CONVERSION C ₃ ClF ₇	% SELECTIVITY HFC-227ea
	0.1	94.90	97.31
	0.2	93.87	97.31
	0.3	84.70	97.13
	0.96	80.90	97.92
	1.03	79.94	99.35
	1.05	79.98	96.91
450ppm H ₂ O	RUN TIME (days)	% CONVERSION C ₃ ClF ₇	% SELECTIVITY HFC-227ea
	0.1	93.67	95.61
	0.7	96.63	96.00
	0.8	95.53	95.79
	1.1	90.69	97.30
	1.7	78.82	97.15
	2.1	81.26	97.72
	3.0	49.15	95.84
	4.1	44.07	78.73
0.29% H ₂ O	RUN TIME (days)	% CONVERSION C ₃ ClF ₇	% SELECTIVITY HFC-227ea
	0.1	95.81	96.09
	0.3	98.40	95.54
	1.2	98.36	96.40
	1.3	98.40	96.44
	1.3	98.31	96.26
	1.3	96.58	96.13
	4.1	96.53	96.30
	4.2	95.88	95.76
	4.3	95.87	95.89
	4.3	95.77	95.74
	5.0	96.48	95.78
	5.1	94.84	95.79
	5.2	92.59	95.36
	5.3	91.89	97.39

	6.2	89.60	97.32
	6.3	91.18	97.44
	6.3	90.91	98.14
	7.0	85.48	97.10
	7.1	83.84	97.22
	7.3	79.20	97.20
	7.3	77.89	97.13
	8.0	69.32	97.10
	8.2	71.62	97.04
	8.3	76.70	97.17
	8.3	80.16	97.50
	11.0	60.41	96.61
	11.0	58.41	96.41
	11.2	56.68	96.36
	11.9	57.05	96.40
	12.1	55.97	96.35
	12.3	55.96	96.33
	12.9	54.04	96.22
	12.9	54.30	96.22
0.8% H2O	RUN TIME	%	%
	(days)	CONVERSION	SELECTIVITY
		C ₃ ClF ₇	HFC-227ea
	0.0	90.10	94.47
	0.7	93.60	95.35
	0.8	94.19	95.81
	1.0	92.39	95.65
	1.9	99.60	96.96
	2.0	96.71	96.59
	4.7	99.73	96.00
	4.8	98.96	97.89
	5.0	97.93	96.00
	5.0	98.16	96.10
	5.8	98.27	96.08
	6.0	97.96	95.95
	6.9	96.76	95.64
	7.8	90.03	94.96
	8.7	96.52	95.42
	9.0	94.70	95.20
	11.7	97.19	97.90
	12.0	93.80	97.45
	12.8	91.60	97.51
	13.0	91.49	97.48
	14.0	96.78	96.04
	15.0	95.11	95.83
	15.1	94.57	94.96

To demonstrate the increased catalyst life utilizing water in the dehydrohalogenation reaction according to this invention, catalyst, H₂ and C₃ClF₇ were prepared as described above with the addition of water as demonstrated in Table

17 above. It is clearly evident, particularly from Fig. 7, that the addition of water significantly increases catalyst life without affecting the conversion and selectivity.

Like Steps I, II and III control and reduction of the undesired isomer in Step IV can be achieved by selective reaction. Example 18 demonstrates this isomer control throughout the entire process when Steps I-IV are utilized in sequence. Of course the combination of the steps of the present invention include the following combinations: I, II and III (production of essentially isomerically pure CFC-217ba); and I, II and IV (production of essentially isomerically pure HFC-227ea); and I and II (production of essentially isomerically pure CFC-216aa). Data from a variety of sources has all shown that even at 90% conversion there is effective reduction of the isomer content.

Example 18: Steps I-IV:

Reactors of the type described in the previous example were placed in series and prepared as previously described. The specific reaction conditions are denoted in the Table 16 below.

Table 16. Isomer Selectivity in Steps I-IV

Control of the Formation of CFC-216aa Steps I and II		Reaction Conditions			Results (%)			
		Step I Reactor Temperature (C)	HF/Cl ₂ /Propane	Contact Time (s)	Step II Reactor Temperature (C)	Additional HF Added (mole)	Contact Time (s)	Selectivity to Usable F-Compounds
Chromium Oxide Catalyst								
A		200	5/8.1/1	15.3	450	10.3	4.85	CFC-216aa 54.3 CFC-216ba 13 CFC-217ca 91.2
B		200	5.22/8.78/1	10.9	450	12	8.9	N/D* 96.3
Isomer Reductions								
Step III: As a Function of Conversion		Results (%)						
Reaction Conditions								
Chromium Oxide Catalyst		Reactor Temperature (C)	HF/ HFC-216aa	Starting % CFC-216ba	Conversion	Selectivity	CFC-216aa	CFC-217ba CFC-217ca
A		450	4.2	1.34	38	56	66.17	0.56 16.12 0.023
B		480	3.7	1.34	48	71	55.07	0.55 30.47 0.13
C		550	6	1.34	90	87	11.73	0.17 79.15 0.47
Step IV: As a Function of Conversion								
All Runs: 0.5% Pd/Al, Contact Time 21 sec, H ₂ :CFC-217ba 1.4:1								
Starting Material % Composition:								
CFC-217ba 99.82378								
CFC-217ca 0.03389								
Reaction Conditions		Starting Material % Composition:						
Results (%)		CFC-217ba 97.25107 CFC-217ca 1.07103						
Reaction Conditions		Results (%)						
Reactor Temperature (C)		Reactor Temperature (C)						
80		Conversion	CFC-217ba	CFC-217ca	HFC-227ca	HFC-227ca	CFC-217ca	HFC-227ca
100		1.27	98.72826	0.03504	1.14277	0.0022	4.06	95.93715
125		8.64	91.3592	0.03461	8.45215	0.00538	12.14	87.86218
150		43.53	56.46954	0.0343	43.2857	0.00871	51.66	48.342
185		72.43	27.57251	0.03347	72.12256	0.01052	83.01	16.99374
		98.27	1.73023	0.01784	97.29827	0.02215	97.26	2.74047
							98.99	1.01341
							0.4536	94.3088
								0.00619
								0.01684
								0.08311
								0.20022
								0.5128
								0.67959

*n/d = Not detected

As Table 16 above demonstrates, the selectivity for a desired isomer at each step carries through when the steps are combined. It is apparent that the four step process may likewise produce HFC-227ea via three steps by performing heretofore, Step IV following Step II. As shown above in Table 16 CFC-217ba is produced following Step II.

According to another aspect of the present invention, a process is provided for the separation of a mixture of isomers of HFC-227ea and HFC-227ca. This mixture can come from different sources, however, it is contemplated the mixture will stem from a hydrodehalogenation reaction as described above. According to one embodiment of the present invention a mixture of these isomers is combined with a chlorofluorocarbon. Preferably, the chlorofluorocarbon is C_3ClF_7 . This solution comprising the HFC-227 isomers and the chlorofluorocarbon are fed to a multiple stage distillation column operated under conditions such that HFC-227ea can be effectively distilled as a pure isomer. Distillation as it is known to those skilled in the art is a separation process in which a liquid is converted to a vapor and the vapor then condensed to a liquid. The latter is referred to as the distillate and the liquid material being vaporized is the charge or distillant. Distillation is thus a combination of the evaporation, or vaporization, and condensation.

The usual purpose of distillation is purification or separation of the components of the mix. This is possible because the composition of a vapor is usually different from that of the liquid mix from which it is obtained. Alcohol has been so purified for generations to separate it from water, fuel oil, and aldehydes produced in the fermentation process. Gasoline, kerosene, fuel oil, and lubricating oil are produced from petroleum by distillation. It is the key operation in removing salt from sea water. Regrettably, isomeric mixtures cannot typically be separated by distillation.

Embodiments of the present isomer separation process include the use of a ratio of chlorofluorocarbon to HFC-227ea from about 0.1 to about 10 and preferably about 1 to about 7. Upon distillation of this mixture essentially pure HFC-227ea is recovered as the distillate. The apparatus necessary to conduct this process will be apparent to those skilled in the art. Fractional distillation columns known in the industry will be readily useful to perform the process of the present invention.

Example 19: Distillation Separation of HFC-227ea from HFC-227ca:

To demonstrate the separation of HFC-227 isomers, a standard distillation apparatus was utilized and configured according to the parameters shown in Tables 17 and 18 below. As indicated, Table 17 demonstrates distillation with a chlorofluorocarbon and Table 18 demonstrates distillation without a
5 chlorofluorocarbon.

Table 17. Distillation with C₃ClF₇

Column Conditions						
	Temperature (°C)			Take Off (g/min)		
Pressure (psig)	Overhead	Bottom	Feed (g/min)	Overhead	Bottom	Reflux Ratio
61.8	29.4	36	2.93	2.21	0.45	25

Separation Results-GC Profiles

	HFC-134a	FC-218	HFC-227ca	HCFC-124	HFC-227ea	HFC-236fa	Unknown	CFC-217ba	CFC-217ca
Feed	0.00258	0.00987	0.07504	0.01	83.33046	0.159881	0.11694	16.11326	0.14152
Overhead Take Off	0.00295	0.00392	0.01548	nd	99.97741	nd	nd	0.00573	nd
Bottom Take Off	nd	nd	0.12677	0.01923	57.10056	0.45827	0.30565	41.63464	0.35488

nd = not detected

Ratio HFC-227ea/HFC-227ca	Feed	1110
	Overhead	6458
	Bottom	450
Isomer Reduction Ratio (Overhead/Feed)		5.8

Table 18. Distillation without C₃ClF₇

Column Conditions						
	Temperature (°C)			Take Off (g/min)		
Pressure (psig)	Overhead	Bottom	Feed (g/min)	Overhead	Bottom	Reflux Ratio
45.5	21.8	22.4	3.591	3.461	0.45	23

Separation Results-GC Profiles

	HFC-134a	FC-218	HFC-227ca	HCFC-124	HFC-227ea	HFC-236fa	Unknown	CFC-217ba	CFC-217ca
Feed	0.00296	0.0687	0.0271	nd	99.95139	nd	nd	0.00928	nd
Overhead Take Off	0.00328	0.00671	0.01195	nd	99.98003	nd	nd	nd	nd
Bottom Take Off	nd	nd	0.07773	nd	99.86733	nd	nd	0.0549	nd

nd = not detected

Ratio HFC-227ea/HFC-227ca	Feed	3688
	Overhead	8367
	Bottom	1285
Isomer Reduction Ratio (Overhead/Feed)		2.3

As shown in Tables 17 and 18, the addition of a chlorofluorocarbon significantly increases the ability, through distillation, to separate the isomers of HFC-227.

- 5 The present invention also provides a process that selectively destroys undesired isomers, thereby increasing the overall isomeric purity in a mixture of isomers. According to one embodiment, this process includes providing a mixture of C-3 chlorofluorinated isomers. In another embodiment of the present invention, the C-3 chlorofluorinated isomers are CFC-216aa and CFC-216ba. In still another
- 10 embodiment of the present invention, the C-3 chlorofluorinated compound isomers are CFC-217ba and CFC-217ca. Other isomer mixtures that can be purified according to the present invention will be apparent to those skilled in the art.

In accordance with the present invention, chlorofluorinated isomers are heated in the presence of a catalyst to a sufficient temperature to reduce the amount of at least one of the chlorofluorinated isomers. The isomers are heated in the presence of a catalyst in like fashion to the reaction Steps I, II, and III described above.

- 5 According to one embodiment the catalyst used is a chromium containing catalyst. A suitable temperature to increase isomeric purity has been found to be from about 250°C to about 350°C. A more preferred temperature is about 280°C. By way of non-limiting example embodiments of this invention will now be demonstrated.

Example 20: Selective destruction of CFC-216ba:

- 10 In accordance with the present invention, a mixture of CFC-216aa and CFC-216ba was provided having a relative ratio of CFC-216aa to CFC-216ba of 96:1. This mixture was heated in the presence of a pre fluorinated Chrom-gel® (provided by Englehard) catalyst at various temperatures outlined below with the results shown in Table 19 below.

Table 19. Selective Destruction of CFC-216ba Isomer

Reaction Temperature(°C)	Relative Ratio of CFC-216aa:CFC-216ba
325	257:1
250	325.03:1
250	309.53:1

- 15 As can easily be seen from Table 19 the process according to the present invention effectively doubled the ratio of preferred isomer, CFC-216aa, to the undesired isomer, CFC-216ba. The differences between the ratio determinations at 250° C are believed to be acceptable analytical error.

To demonstrate still another embodiment of the present invention, non-limiting example 21 is provided.

Example 21: Selective Destruction of CFC-217ca:

In accordance with the present invention, a mixture of CFC-217ba and CFC-
5 217ca was provided having a relative ratio of CFC-217ba to CFC-217ca of 81:1.
This mixture was heated in the presence of a pre-fluorinated Chrom-gel® catalyst at various temperatures outlined below with the results shown in Table 20 below.

Table 20. Selective Destruction of CFC-217ca
Isomer

Reaction Temperature(°C)	Relative Ratio of CFC-217ba:CFC-217ca
250	252.79:1
280	548.11:1

As can easily be seen from Table 20, the process according to the present invention effectively at least doubled the ratio of the preferred isomer, CFC-217ba, to the undesired isomer, CFC-217ca and in some instances more than quadrupled the ratio. Once purified in this fashion the resulting isomer is an excellent reactant for hydrodehalogenation according to Step IV of the present invention.

In keeping with the selective destruction process previously described, a process for selectively halogenating specific isomers within an isomeric mixture is also provided. Isomer selective reactions play an important role when isomerically pure products are desired. According to one embodiment of the present invention a mixture of C-3 fluorinated isomers is provided and these isomers are contacted with Cl₂ in the presence of a catalyst at a sufficient temperature to halogenate at least one isomer.

According to one embodiment of the present invention the mixture of C-3 fluorinated isomers contains HFC-227ea and HFC-227ca. It is contemplated that other hydrohalogenated compounds may be selectively halogenated according to this invention as well. Hydrohalogenated compounds suited for selective halogenation according to this invention will be obvious to those skilled in the art.

According to still another embodiment of the present invention the catalyst is activated carbon. The specific type and preparation of the catalyst used to selectively halogenate are consistent with those catalysts described above in Steps I-IV.

One aspect of the invention provides for the heating of the isomeric mixture to a sufficient temperature. According to one embodiment the temperature is from

about 200°C to about 350°C. According to a more preferred embodiment, the temperature is about 300°C.

According to still another embodiment of the present invention the molar ratio of Cl₂ to the isomeric mixture is from about 0.16:1 to about 3:1 and preferably about
5 2.5.

By way of non-limiting example 22, embodiments of the present invention will now be demonstrated.

Example 22: Selective Halogenation of HFC-227ea:

The specific quantities and types of reactants and the condition of the reactor
10 utilized to demonstrate this invention are shown in Table 21 below. The reaction products were monitored for the isomers of CFC-217.

Table 21. Selective Chlorination of HFC-227ea

Starting Material % Composition: CFC-227ea 99.8678 CFC-227ea 0.0749						
Reaction Conditions				Results (%)		
Activated Carbon	Reactor Temperature (C)	Contact Time (s)	Cl ₂ /HFC-227 Molar	Conversion	Selectivity	CFC-227ea CFC-217ea
250		13.3	2.01	24.49	98.85	0.0628 0.0219
300		12.8	1.81	54.46	98.91	0.064 0.0223
325		11.9	1.48	48.15	96.78	0.0744 0.0217
325		21.9	2.69	98.91	97.91	n/d* 0.0767
350		13.2	1.97	65.51	96.2	0.0548 0.0281
325		22.3	2.91	98.14	98.25	0.0063 0.0751
200		38.5	0.16	3.23	71.21	0.0981 0.0055
300		21.8	0.55	44.81	96.51	0.0701 0.0211
*n/d = non-detectable						
Starting Material % Composition: CFC-227ea 99.5013 CFC-227ea 0.1411						
Reaction Conditions				Results (%)		
Activated Carbon	Reactor Temperature (C)	Contact Time (s)	Cl ₂ /HFC-227 Molar	Conversion	Selectivity	CFC-227ea CFC-217ea
300		16.3	0.174692697	18.3	96.8	0.1255 0.0113
300		15.8	0.34	46.8	98.6	0.0899 0.0414
300		14.8	0.328435145	55.6	98.5	0.0829 0.0531
300		26.9	0.84	79.2	98.7	0.0341 0.093

As Table 21 demonstrates, the present invention can be used to even further reduce the content of the undesired isomer. It is contemplated that once reduced the more isomerically pure reaction product can be recycled or further refined.

Additional objects, advantages, and other novel features of the invention will
5 become apparent to those skilled in art upon examination of the foregoing or may be learned with practice of the invention. The foregoing description of the preferred embodiments of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed. Obvious modifications or variations are possible in the light of the
10 above teachings. Embodiments were chosen and described to provide the best illustrations of the principals of the invention and their practical application, thereby enabling one of ordinary skill in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. All such modifications and variations are within the scope of the
15 invention as determined by the appended claims when interpreted in accordance with the breadth to which they are fairly, legally and equitably entitled.

What is claimed is:

1. A method for preparing CFC-216aa by reacting non perhalogenated hydrocarbons having at least three carbon atoms with at least HF in the presence of a catalyst, the improvement comprising
 - 5 (a) reacting non perhalogenated hydrocarbons having at least three carbon atoms at a first temperature to form a perhalogenated intermediate, and
 - (b) reacting the perhalogenated intermediate at a second temperature to form CFC-216aa.
2. The process of claim 1 further comprising
 - 10 (c) contacting the CFC-216aa with the HF in the presence of a catalyst at a third temperature to form CFC-217ba.
3. The process of claim 2 further comprising
 - (d) contacting the CFC-217ba with H₂ in the presence of a catalyst at a fourth temperature to produce HFC-227ea.
- 15 4. The process of claims 1, 2, or 3 wherein the first temperature is at least about 150°C, the second temperature is at least about 300°C, the third temperature is at least about 200°C and the fourth temperature is at least about 30°C.
5. The process of claims 1, 2, or 3 wherein the first temperature is from about 150°C to about 450°C, the second temperature is from about 300°C to about
20 550°C, the third temperature is from about 200°C to about 550°C and the fourth temperature is from about 30°C to about 275°C.
6. The process of claims 1, 2, or 3 wherein the first temperature is about 220°C, the second temperature is about 470°C, the third temperature is about 470°C and the fourth temperature is about 185°C.
- 25 7. The process of claims 1, 2, or 3 wherein the molar ratio of HF:Cl₂ used in step (a) is from about 0.75:1 to about 8:1.
8. The process of claims 1, 2, or 3 wherein the molar ratio of HF:Cl₂ used in step (a) is about 4:1.

9. The process of claims 1, 2, or 3 wherein the molar ratio of Cl_2 to C-3 reactants used in step (a) is from about 8:1 to about 10:1.

10. The process of claims 1, 2, or 3 wherein the molar ratio of Cl_2 to C-3 reactants used in step (a) is about 8.2:1.

5 11. The process of claim 1, 2, or 3 wherein the molar ratio of HF to C-3 reactants used in step (a) is from about 6:1 to about 64:1.

12. The process of claims 1, 2, or 3 wherein the molar ratio of HF to C-3 reactants used in step (a) is about 35:1.

10 13. The process of claims 1, 2, or 3 wherein the molar ratio of HF to perhalogenated compounds used in step (b) is from about 6:1 to about 64:1.

14. The process of claims 1, 2, or 3 wherein the molar ratio of HF to perhalogenated compounds in step (b) is about 30:1.

15. The process of claims 1, 2, or 3 wherein the molar ratio of HF to CFC-216aa used in step (c) is from about 1:1 to about 30:1.

15 16. The process of claims 1, 2, or 3 wherein the molar ratio of HF to CFC-216aa used in step (c) is about 10:1.

17. The process of claims 1, 2 or 3 wherein the molar ratio of H_2 to CFC-217ba used in step (d) is from about 0.2:1 to about 10:1.

20 18. The process of claims 1, 2, or 3 wherein the molar ratio of H_2 to CFC-217ba used in step (d) is about 1.2:1.

19. The process of claims 1, 2, or 3 further comprising the addition of water in step (d).

20. The process of claims 1, 2 or 3 wherein the water is present in an amount from about 0.04 to about 12 percent by weight of the CFC-217ba.

25 21. The process of claims 1, 2 or 3 wherein the water is about 0.8 percent by weight of the CFC-217ba.

22. The process of claims 1, 2 or 3 further comprising the addition of Cl_2 in step (b).
23. The process of claims 1 or 2 wherein the catalyst chromium and a catalyst support.
- 5 24. The process of claim 3 wherein the catalyst of step (d) comprises Pd and a catalyst support.
25. The process of claims 1, 2, or 3 further comprising the addition of diluent in at least one of steps (a)-(d).
- 10 26. The process of claims 1, 2, or 3 wherein, in at least one of steps (a)-(c), underfluorinated products are recycled to at least one of steps (a)-(c).
27. A process for extending the catalyst life of a hydrodehalogenation reaction, the improvement comprising the addition of water to the reaction.
28. The process of claim 27 wherein CFC-217ba is a reactant.
- 15 29. The process of claims 27 or 28 wherein the ratio of H_2 to halogenated organic compound is from about 0.2:1 to about 10:1.
30. The process of claims 27 or 28 wherein the ratio of H_2 to halogenated organic compound is about 1.2:1.
31. The process of claims 27 or 28 wherein the H_2O is from about 0.04 to about 12 percent by weight of the halogenated organic compound.
- 20 32. The process of claims 27 or 28 wherein the H_2O is about 0.8 percent by weight of the halogenated organic compound.
33. The process of claims 27 or 28 wherein a catalyst containing a metal is utilized.
- 25 34. The process of claims 27 or 28 wherein a catalyst comprising Pd and a catalyst support is utilized.

35. A process for purifying HFC-227ea from a mixture containing HFC-227ea, HFC-227ca and a chlorofluorocarbon the improvement comprising distilling the mixture to obtain essentially pure HFC-227ea.
36. The process of claim 35 wherein the chlorofluorocarbon comprises
5 C₃ClF₇.
37. The process of claims 35 or 36 wherein the chlorofluorocarbon to HFC-227ea ratio is from about 0.1 to about 10.
38. The process of claims 35 or 36 wherein the chlorofluorocarbon to HFC-227ea ratio is about 1:2.
- 10 39. A process for purifying C-3 chlorofluorinated halogenation reaction products from a mixture containing C-3 chlorofluorinated halogenation reaction products and HF the improvement comprising: adjusting the temperature of the mixture to produce a mixture having an essentially pure HF phase and an essentially pure C-3 chlorofluorinated halogenation reaction products.
- 15 40. The process of claim 39 wherein the HF or C-3 chlorofluorinated halogenation reaction products are removed to produce essentially pure HF or C-3 chlorofluorinated halogenation reaction products.
41. The process of claims 39 or 40 wherein the C-3 chlorofluorinated compounds have at least six fluorine atoms.
- 20 42. The process of claims 39 or 40 wherein the temperature is from about -30°C to about -10°C.
43. The process of claims 39 or 40 wherein the temperature is about -20°C.
- 25 44. A process for purifying C-3 chlorofluorinated compounds having at least six fluorine atoms from a mixture containing C-3 chlorofluorinated compounds having at least six fluorine atoms and chlorofluorinated compounds having less than six fluorine atoms the improvement comprising:

contacting the mixture with water and adjusting the temperature of the mixture to produce an upper gas phase containing the C-3 chlorofluorinated compounds and a lower liquid phase.

5 45. The process of claim 44 wherein the lower liquid phase comprises a top primarily aqueous phase and a bottom phase comprising chlorofluorinated compounds having less than six fluorines.

46. The process of claims 44 or 45 wherein the C-3 chlorofluorinated compounds having at least six fluorine atoms comprises CFC-216aa.

10 47. The process of claims 44 or 45 wherein the temperature is from about 25°C to about 75°C.

48. The process of claims 44 or 45 wherein the temperature is about 50°C.

49. The process of claims 44 or 45 wherein the water includes a basic compound.

50. The process of claims 44 or 45 wherein water includes KOH.

15 51. A process of purifying C-3 chlorofluorinated halogenation reaction products from a halogenation reaction product comprising C-3 chlorofluorinated compounds, HCl and HF, the improvement comprising adjusting the temperature of the halogenation reaction product to a temperature to produce a gas phase comprising HCl, an upper liquid phase containing HF and a lower liquid phase containing
20 essentially HF free C-3 chlorofluorinated compounds.

52. The process of claim 51 wherein the C-3 chlorofluorinated compounds comprise CFC-217ba.

53. The process of claims 51 or 52 wherein the temperature is from about 20°C to about 75°C.

25 54. The process of claims 51 or 52 wherein the temperature is about 25°C.

55. A process for increasing the isomeric purity of a mixture containing at least two C-3 chlorofluorinated isomers, the improvement comprising heating the mixture in the presence of a catalyst to increase the concentration of at least one of isomers in the mixture.

56. The process of claim 55 wherein the C-3 chlorofluorinated compound isomers comprise CFC-216aa and CFC-216ba.

57. The process of claim 55 wherein the C-3 chlorofluorinated compound isomers comprise CFC-217ba and CFC-217ca.

5 58. The process of claims 55, 56, or 57 wherein the catalyst comprises a chromium containing catalyst.

59. The process of claims 55, 56, or 57 wherein the temperature is from about 250°C to about 350°C.

10 60. The process of claims 55, 56, or 57 wherein the temperature is about 280°C.

61. A process for selectively halogenated isomers of an isomeric mixture the improvement comprising contacting the mixture with Cl₂ in the presence of a catalyst at a sufficient temperature to halogenate at least one isomer.

15 62. The process of claim 61 wherein the isomeric mixture comprises HFC-227ea and HFC-227ca.

63. The process of claims 61 or 62 wherein the catalyst comprises activated carbon.

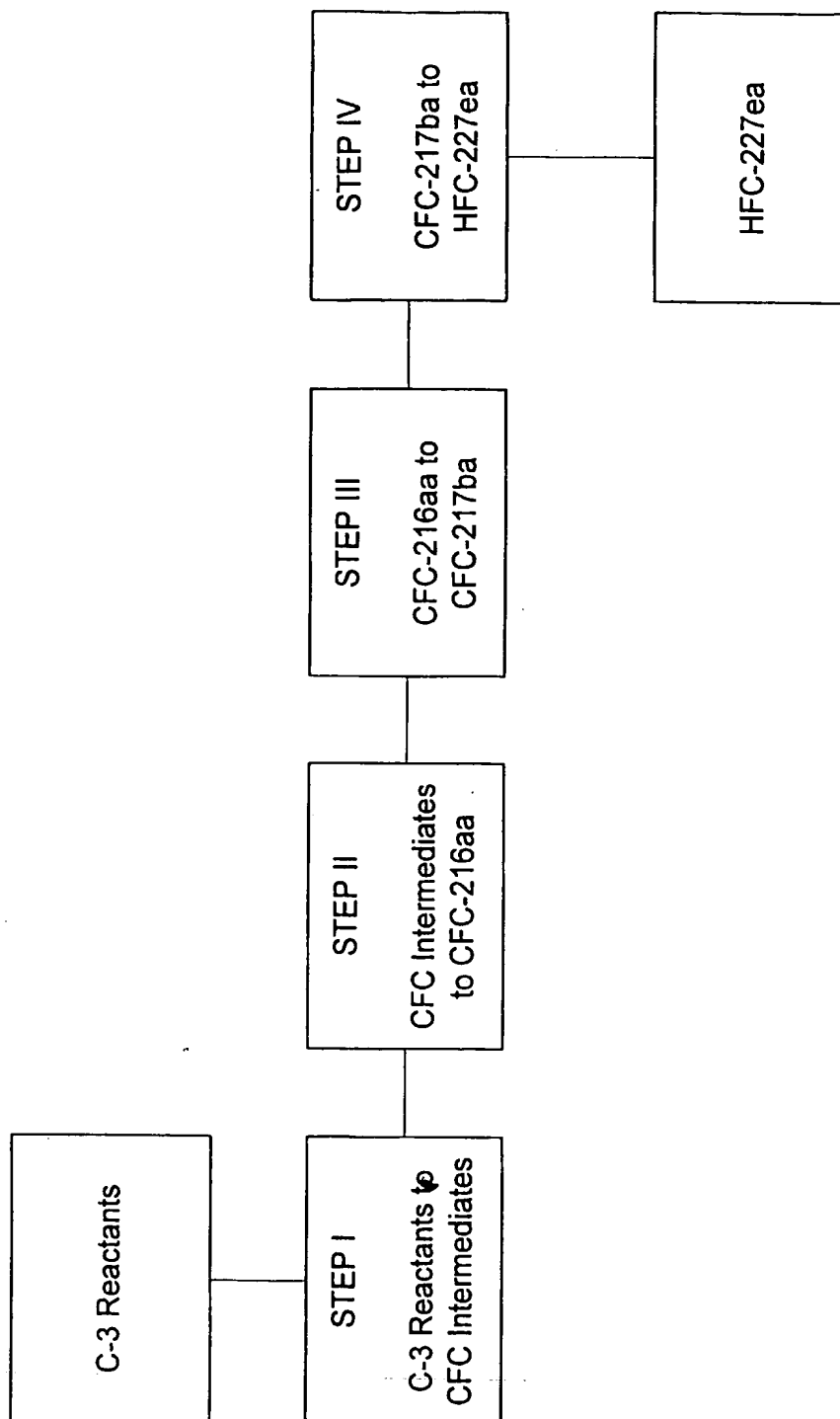
64. The process of claims 61 or 62 wherein the temperature is from about 200°C to about 350°C.

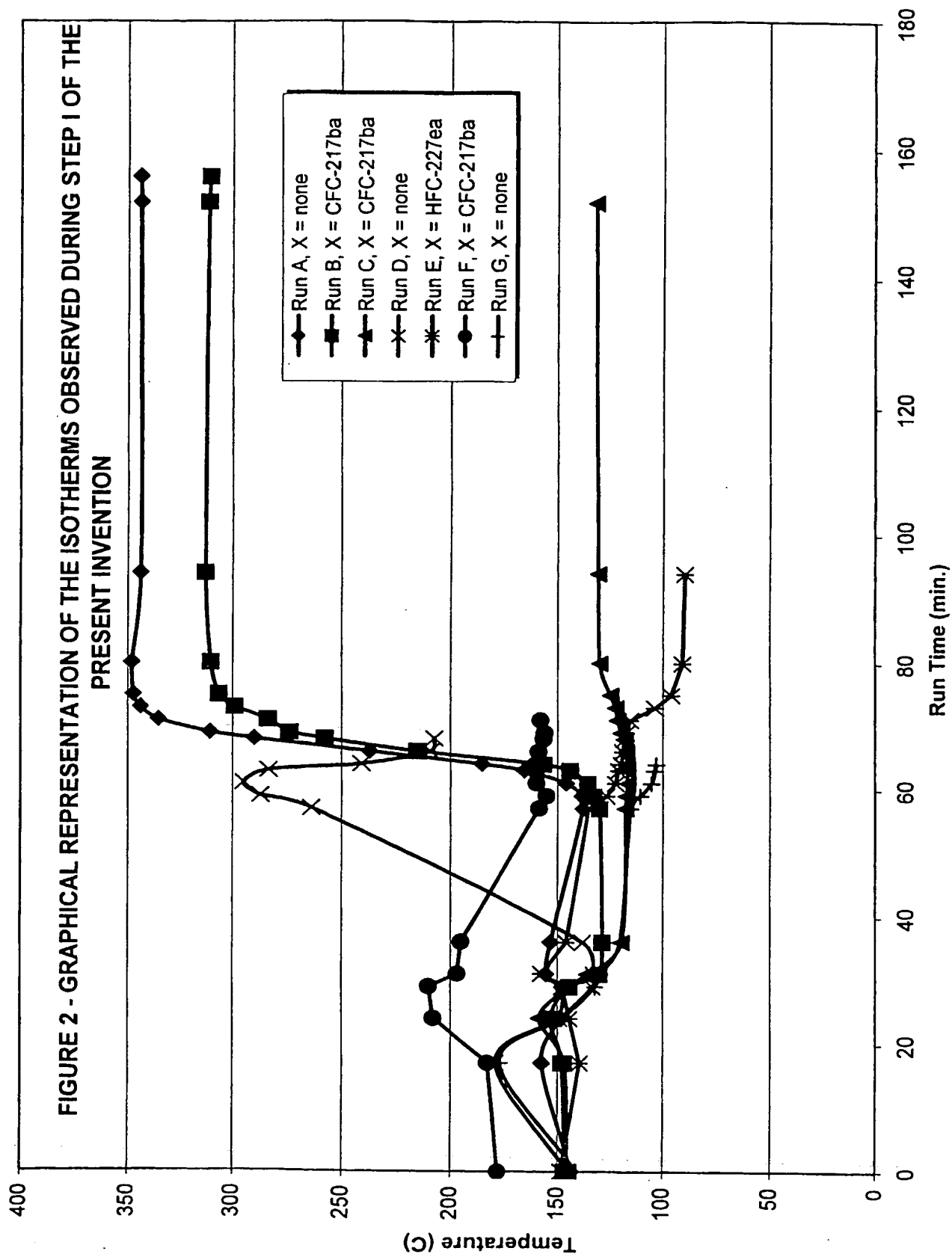
20 65. The process of claims 61 or 62 wherein the temperature is about 300°C.

66. The process of claims 61 or 62 wherein the molar ratio of Cl₂ to isomeric mixture is from about 0.16:1 to about 3:1.

25 67. The process of claims 61 or 62 wherein the molar ratio of Cl₂ to isomeric mixture is about 2.5:1.

FIGURE 1





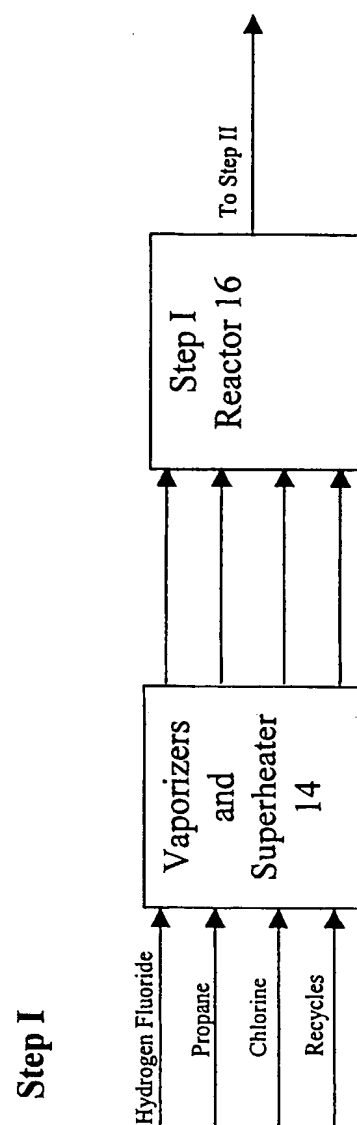


FIGURE 3

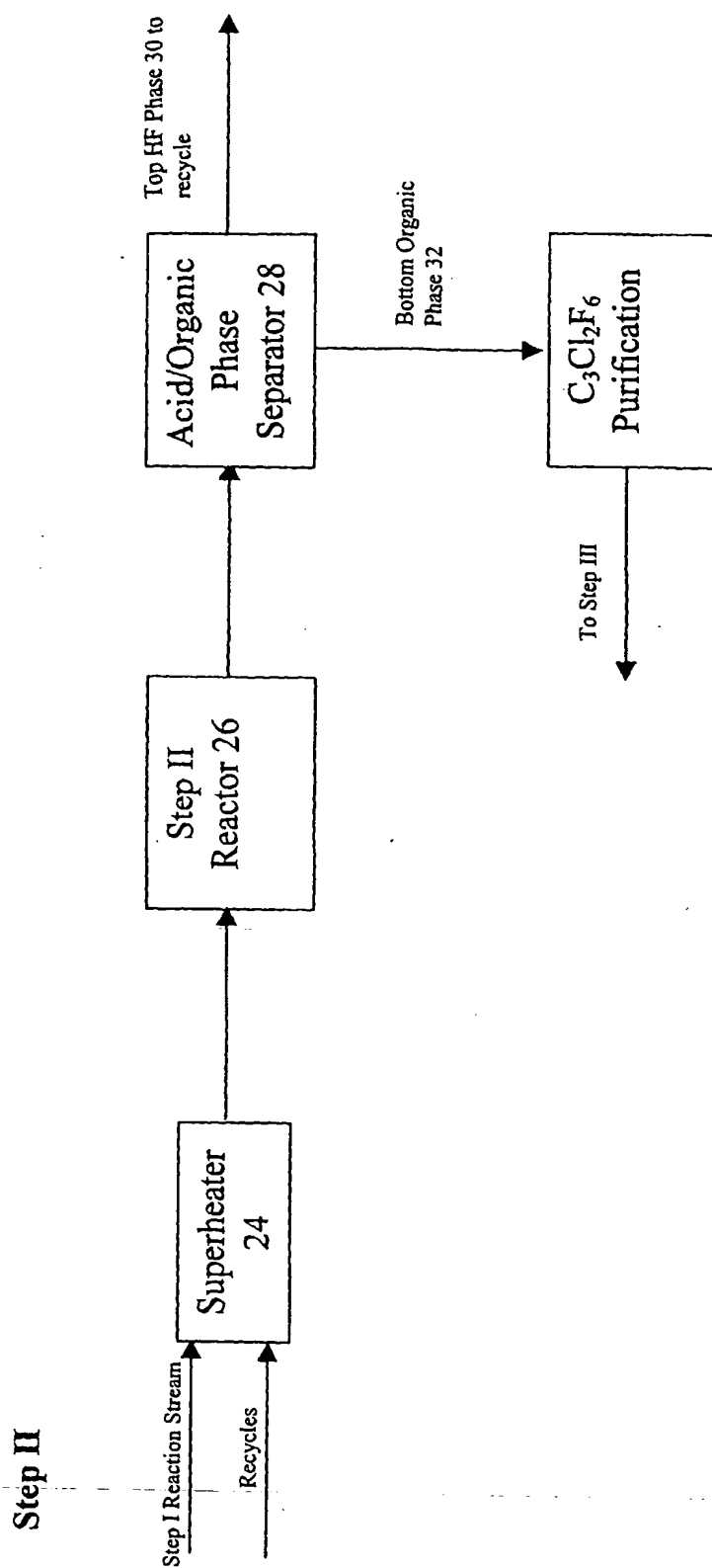


FIGURE 4

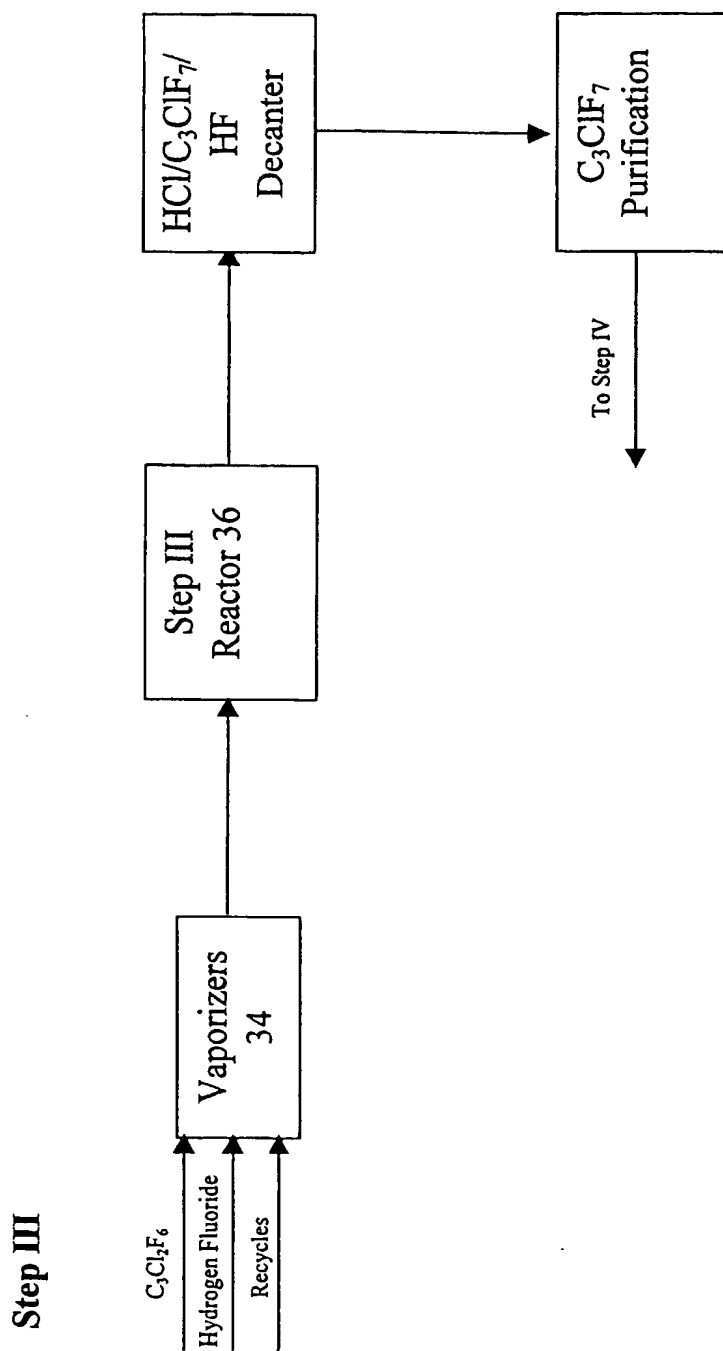


FIGURE 5

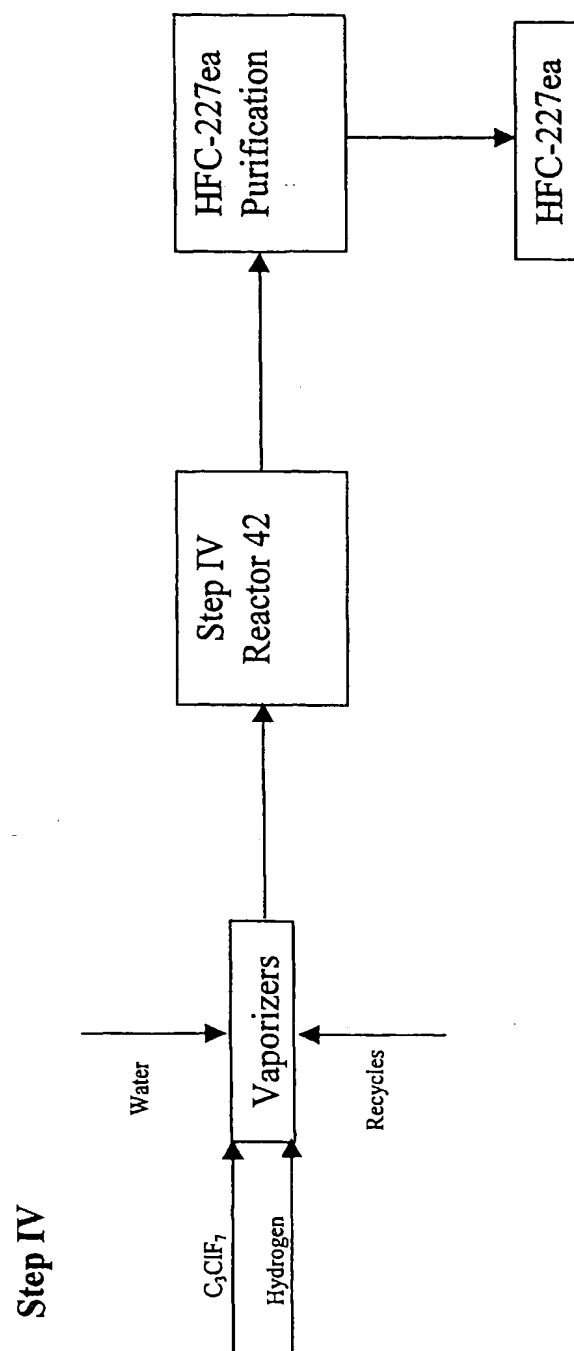
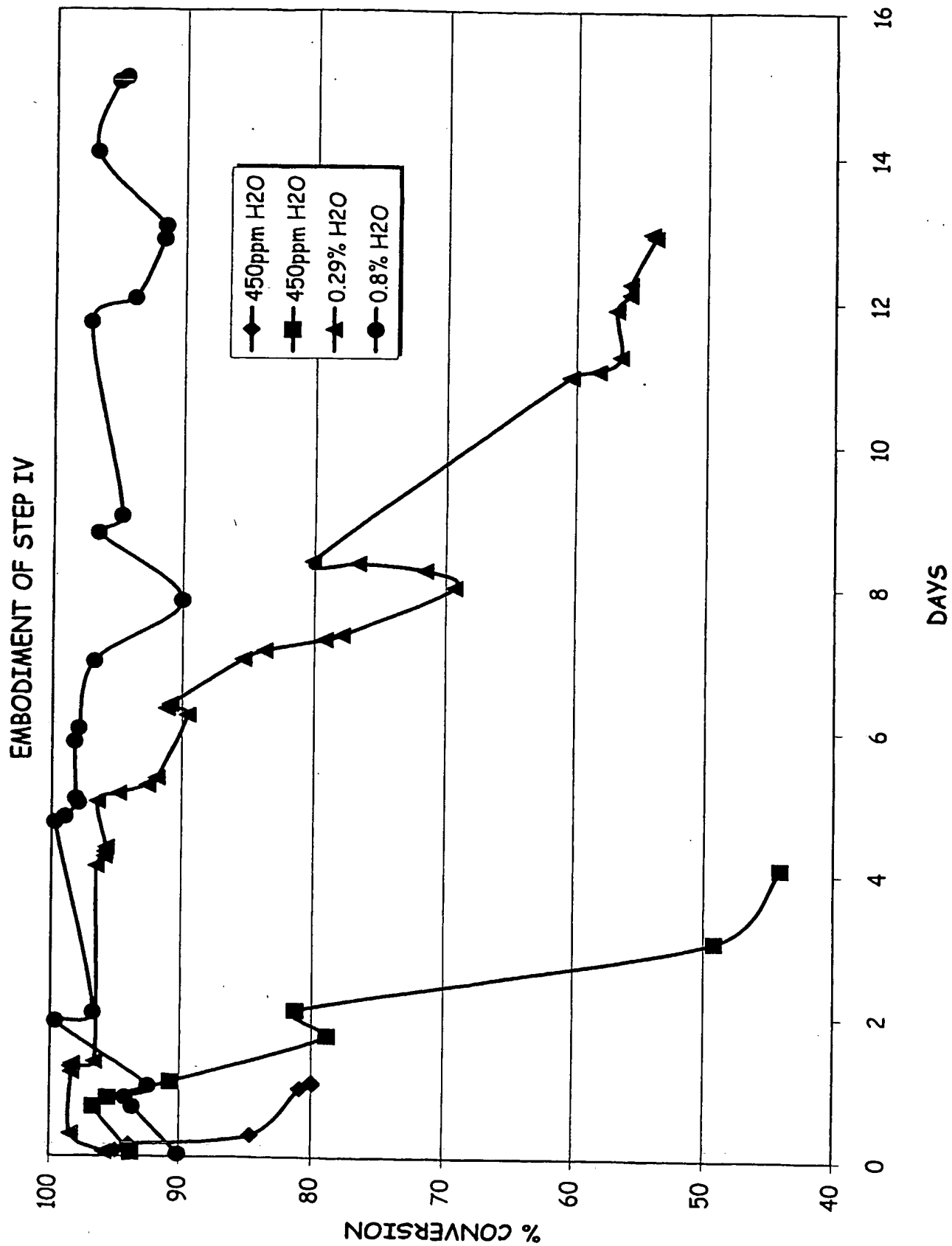


FIGURE 6

FIGURE 7 - GRAPHICAL REPRESENTATION of the INCREASED CATALYST LIFE OBSERVED in an EMBODIMENT OF STEP IV



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(71) Applicant: PCBU SERVICES, INC. [US/US]; 300
Delaware Avenue, Suite 1269, Wilmington, DE 19801
(US).

(72) Inventors: IKUBO, Yuichi; 2825 Barlow Street, West
Lafayette, IN 47906 (US). OWENS, Stephen; 327 Deer
Creek Trail, White Pine, TN 37890 (US). COHN, Mitchel;
3029 Couthouse, Apt. 2B, West Lafayette, IN 46205 (US).
BRANDSTADTER, Stephan, M.; 3946 N. Washington
Boulevard, Indianapolis, IN 46205 (US). HEDRICK,
Vicki, E.; 9262 South 300 E, Brookston, IN 47923 (US).
BOGGS, Janet, K.; 6922 N 900 E, Brownsburg, IN
46112 (US). CHENGPING CHIEN, John; 3384 Pep-
permill Drive, Apt. 1D, West Lafayette, IN 47906 (US).
SACARIAS, Julie; 908 West 7th Street, El Dorado, AR
71730 (US).

(74) Agent: HYTA, Robert, C.; Wells St. John, P.S., 601 W.
1st Avenue, Suite 1300, Spokane, WA 99201-3828 (US).

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Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a
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- as to the applicant's entitlement to claim the priority of the
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Published:

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For two-letter codes and other abbreviations, refer to the "Guid-
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(54) Title: MATERIALS AND METHODS FOR THE PRODUCTION AND PURIFICATION OF CHLOROFLUOROCARBONS
AND HYDROFLUOROCARBONS

(57) Abstract: Methods and materials are provided for the production of essentially isomerically pure perhalogenated and partially halogenated compounds. One embodiment of the present invention provides a process for the production of essentially isomerically pure CFC-216aa. Other embodiments include processes for the production of CFC-217ba and HFC-227ea. Particular embodiments of the present invention provide separation techniques for the separation of chlorofluorocarbons from HF, from other chlorofluorocarbons, and the separation of isomers of halogenated compounds. Still other embodiments of the present invention provide catalytic synthetic techniques that demonstrate extended catalyst lifetime. In other embodiments, the present invention provides catalytic techniques for the purification of isomeric mixtures.

WO 03/029173 A3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/LU 2/30729

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C17/10 C07C17/20 C07C17/21

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, BEILSTEIN Data, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 043 491 A (BRUHNKE DOUGLAS W ET AL) 27 August 1991 (1991-08-27) cited in the application column 8, line 48 -column 9, line 6; claim 1 column 3, line 20 -column 4, line 9	1,7-14, 22,23, 25,26
Y	---	2-6, 15-19
Y	US 5 068 472 A (BONIFAZ CRISTOBAL ET AL) 26 November 1991 (1991-11-26) column 5, line 52 -column 6, line 10	2-6, 15-18
Y	EP 0 539 989 A (HOECHST AG) 5 May 1993 (1993-05-05) the whole document	2-6, 15-19

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Seufert, G

INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 018 083 A (MANOGUE WILLIAM H ET AL) 25 January 2000 (2000-01-25) cited in the application the whole document ---	1-26
A	US 5 057 634 A (BONIFAZ CRISTOBAL ET AL) 15 October 1991 (1991-10-15) cited in the application the whole document -----	1-16

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-26

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-26

Method for the preparation of 2,2-dichlorohexafluoropropane (CFC-216aa)

2. Claims: 27-34

Process for extending the catalyst life of a hydrodehalogenation reaction

3. Claims: 35-38

Process for the purification of
1,1,1,2,3,3,3-heptafluoropropane (HFC 227ea) from
1,1,1,2,2,3,3-heptafluoropropane (HFC 227ca)

4. Claims: 39-43, 51-54

Process for purifying C-3 chlorofluorinated halogenation reaction products from hydrogen fluoride

Process for purifying C-3 chlorofluorinated halogenation reaction products from hydrogen fluoride and hydrogen chloride

5. Claims: 44-50

Process for purifying C-3 chlorofluorinated compounds having at least six fluorine atoms from chlorofluorinated compounds having less than six fluorine atoms

6. Claims: 55-60

Process for increasing the isomeric purity of a mixture containing at least two C-3 chlorofluorinated isomers

7. Claims: 61-67

Process for selectively halogenating isomers of an isomeric mixture

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 2/30729

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